Agricultural Chemistry

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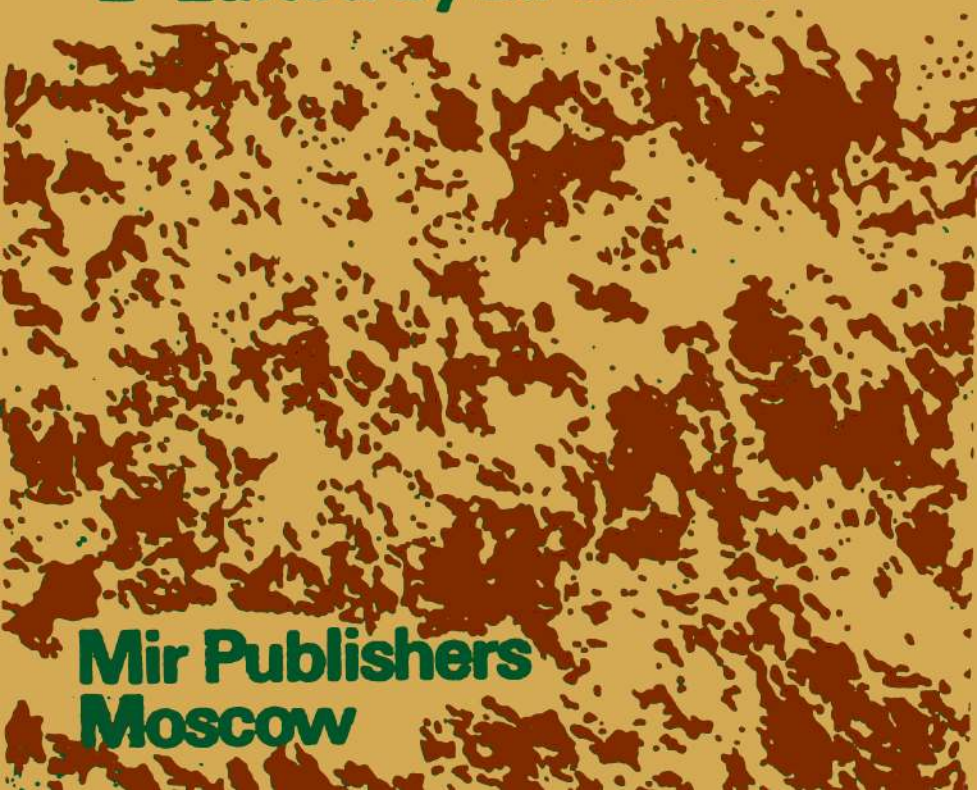

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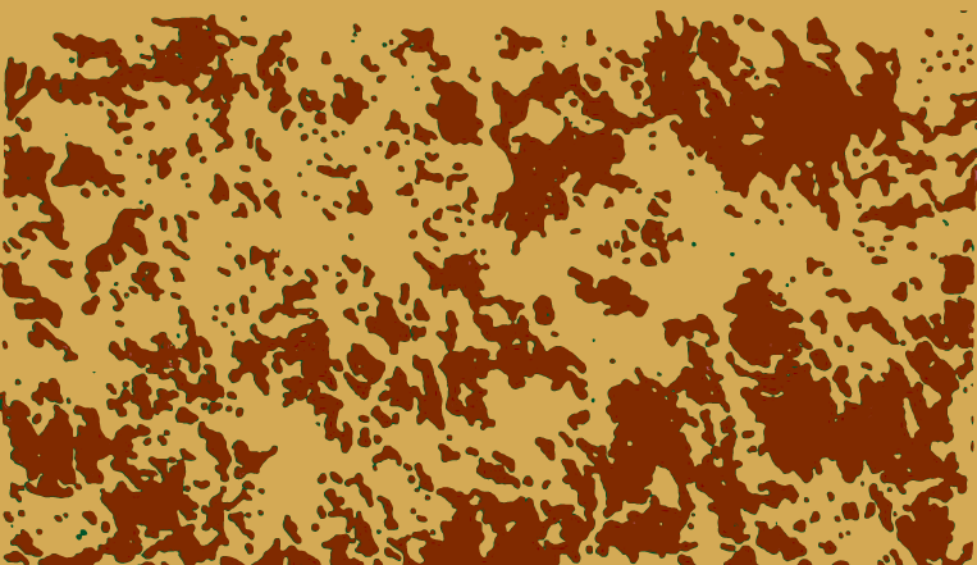

Agri-cultural Chemistry

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Edited by B.A.YAGODIN

Агрохимия

Часть I

Под редакцией Б. А. Ягодина

ИЗДАТЕЛЬСТВО «КОЛОС», МОСКВА

Agri-cultural Chemistry 1

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Introduction

Agricultural chemistry, or agrochemistry for short, is a scientific discipline concerned with the interaction of plants, soil, and fertilizers in the cultivation of farm crops, the cycle of nutrients in agriculture, and the application of fertilizers to improve the yield of crops, their quality, and the fertility of soil.

The eminent Soviet agricultural chemist Academician Pryanishnikov wrote that the objective of agrochemistry is to study the cycle of nutrients in agriculture and find ways to influence the chemical processes occurring in the soil and plants with a view to enhancing the yields of crops or varying their structure. Application of fertilizers is by far the most drastic way of altering this cycle.

Agricultural chemistry aims at providing the optimal plant nutrition conditions, based on the knowledge of the properties of various kinds and forms of fertilizers, their interaction with the soil, as well as definition of the most effective application procedures and schedules. Agrochemistry as a science has been making extraordinary strides, spurred by the exigencies of day-to-day activities and the need to constantly increase the productivity of farm crops through extensive use of inorganic and organic fertilizers, improvements in cultivation techniques, advances in breeding and other sciences.

Speaking about the factors determining the intensification of agriculture, Lenin wrote: "...Expenditure on fertilizers and the value of implements and machinery are the most exact statistical expression of the degree of intensification of agriculture".

Intensification of farm production and steady increases in the yield of crops per hectare are necessary to meet the population's requirements for sufficient amounts of high-quality foodstuffs and raw materials for certain industries. The possibilities to increase farm production by expanding arable areas are strongly limited and, therefore, it is extremely important to use the available land properly and with the highest efficiency possible.

The main task of agriculture is to make an effective use of solar energy in the production of organic matter. Chlorophyll-containing plants provide unique means for accomplishing this task.

Land plants extract from the atmosphere about 20 billion tons of carbon as CO_2 (1300 kg per hectare) annually, the total amount of carbon extracted by all plants, including algae, being in the neighbourhood of 150 billion tons per year. Land plants alone convert each year 4.2^{17} kJ of cosmic energy (light) into assimilation products.

However, the factors of utilization of the photosynthetic active radiation (PAR: λ = 380-720 nm), constituting 47 to 49 per cent of the integrated solar radiation, for production of organic matter are extremely low. Usually, in the case of conventional cultivation, the PAR utilization factors range from 0.5 to 3 per cent. The highest possible PAR efficiency of a truly photosynthetic process in sunlight is 28 per cent. The most intensive accumulation of the biomass, up to 700 kg per day, is observed in phytocenoses under optimal conditions of illumination, temperature, and water supply, as well as high level of inorganic nutrition, and constitutes up to 14 per cent of the daily amount of the PAR energy available to the plants.

Man cannot actively control the flux of solar radiation, nor can he alter other factors involved in the vital activities of plants. Application of fertilizers thus represents a decisive means for enhancing the yielding capacity of crops and improving the cycle of nutrients in agriculture.

The use of inorganic and organic fertilizers forms the basis of chemicalization of agriculture. Their effectiveness is to a great degree dependent on the extent of industrialization of agriculture, overall mechanization, land reclamation, implementation of advances in science, interfarm cooperation, and agro-industrial integration.

The Scope of Agrochemistry. Application of fertilizers increases the content of available nutrients in the soil, whereby the chemical composition of the latter, its physical and other properties are changed. Improvement of inorganic nutrition produces a favourable effect on photosynthesis and intensifies the growth of plants.

Pryanishnikov pointed out that rational application of fertilizers is possible only with due account for all the relevant factors of soil chemistry and plant physiology. He graphically represented the interrelationship between the three main objects of agrochemistry: plant, soil, and fertilizer. This graphic representation has become known in the agrochemical literature as the Pryanishnikov triangle (see Fig. 1). He also emphasized that climatic and all other factors must be taken into consideration in studying the interrelationship between plants, soil, and fertilizers.

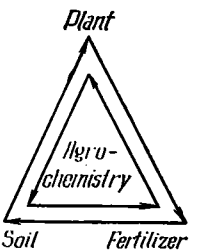


Fig. 1: Pryanishnikov triangle

Green plants produce a dramatic impact on all processes on our planet. Being sustained by autotrophic nutrition, they convert carbon dioxide, water, and mineral salts into most complex organic compounds through the agency of solar energy.

The nutrition of animals and most microorganisms relies on the organic matter photosynthesized by green plants. Plants build up their own mass from water, carbon dioxide, and inorganic nutrients present in the soil which is altered as a result. Their root exudates can convert unavailable forms of some compounds into available forms. Depending on its biological properties, each plant requires a certain amount of moisture, optimal temperatures, various ratios between soil-derived nutrients, and other conditions for adequate support of all its vital activities.

Plants affect the physical properties of the soil by changing its porosity and improving its structure, while its chemical properties are altered as a result of the biological migration of some nutrients into the top layer, induced by the vital activities of plants.

A tangible effect on all soil properties is produced by the organic matter resulting from dying away of the root system and decomposition of the crop residues left in the field after harvesting. Incorporation of fertilizers into the soil changes the ratio and amounts of the individual nutrients present

there, reaction of the soil solution (pH), and the composition of the absorbing complex, as well as activates many microbiological processes (see Fig. 3).

Methods of Agrochemical Research. The theoretical and practical aspects of agrochemistry are studied using various approaches, primarily:

1. Biological methods, including field, greenhouse, and lysimeter experiments.

The biological methods give an insight into the role of individual nutrients in sustaining plants, their optimal ratios and amounts for different crops, and the mechanism of their translocation into plants. Field experiments are conducted to determine the effect of fertilizers on the yield of farm crops, their quality, as well as on soil fertility.

2. Laboratory methods of qualitative and quantitative analysis of soils, plants, and fertilizers.

3. Mathematical methods, including statistical processing of experimental data and mathematical modelling of processes.

4. Biophysical and microbiological methods.

Agrochemistry and Other Sciences. The fundamentals of agrochemistry include the theory of plant nutrition, the major agrochemical properties of soil in the context of plant nutrition and interaction with fertilizers, and properties of fertilizers.

Agrochemistry is closely related to the physiology of plants, concerned with the functions of green plants and vital activities of plant organisms.

Knowledge of plant organism properties underlies the science of agrochemistry. Cultivation of plants and the desire to maximize their yields call for a perfect match between the requirements of a plant organism and the cultivating conditions. The environmental factors are studied by pedology, meteorology, and agrophysics—sciences with which agrochemistry is closely associated.

Agrochemists resort to findings in such disciplines as the genetics and breeding of farm crops, agronomy, agricultural microbiology, and biochemistry. It is hard to define the boundaries between agrochemistry and plant physiology, agrochemistry and biochemistry of plants.

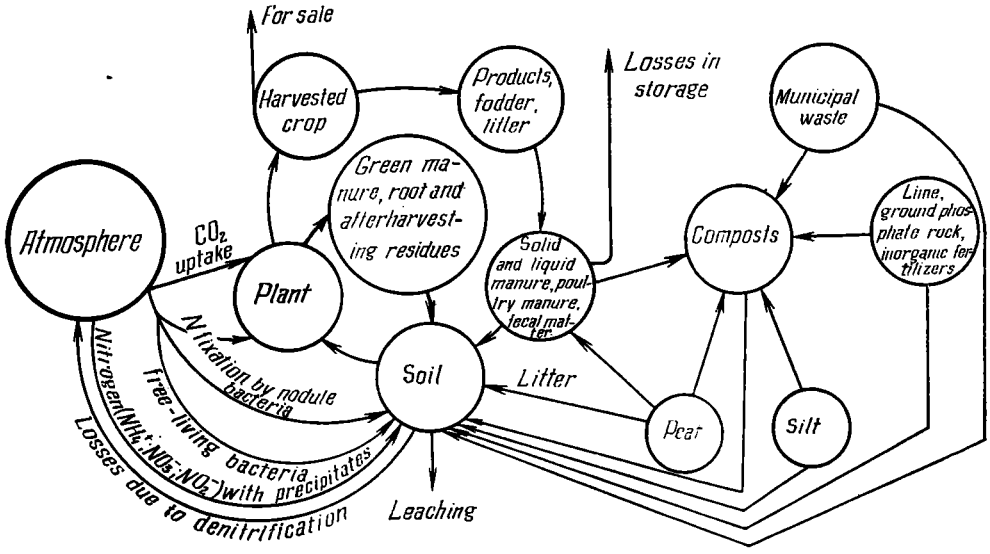


Fig. 2: Nutrient cycle in agriculture

The interrelationship among various disciplines can be illustrated by the scheme proposed by Pryanishnikov as far back as 1906.

Agrochemistry and Other Disciplines

In terms of objects of research		*In terms of methods*		
		Agrochemistry	Agrophysics	Agrobotany
Plant	Plant physiology	Plant chemistry (metabolism)	Physical processes in plants	Physiology of reproduction and morphogenesis
Environment	Pedology Meteorology	Chemistry of soil and atmosphere	Soil physics. Physical phenomena	–
Cultivation	Agronomy	Control over soil chemistry (theory of fertilizers)	Control over physical properties of soil (theory of tillage)	Control over plant growth (growing and breeding)

While using biological, chemical, biochemical, and physical methods as well as morphogenetic laws, the agrochemist must take into account the plant requirements, properties of the environment, and ways to match and vary both.

Soil tillage techniques, care of plants, adequate supply of water and CO_2 (in hothouses), employment of growth retardants and stimulators must be brought strictly in line with the amounts, selection, and application of fertilizers.

If this balance is upset, the effectiveness of all the above procedures may be extremely low.

Many years ago, the fact that yields are rapidly increased by inorganic fertilizers prompted Timiryazev to remark that modern agriculture had reached its current level only owing to agricultural chemistry and physiology of plants.

Agrochemistry is essentially a chemical and biological science. The application of fertilizers in fact involves synthesis of all the procedures adopted in agriculture to maxi-

mize the crop yield. One should not forget, however, about the possible consequences. For instance, improper application of nitrogen fertilizers may lead to contamination of underground water with nitrates. Excess amounts of nitrates in drinking water or such plants as leaf vegetables, greens, and potato where they readily accumulate may harm animal organisms.

The beneficial effect of micronutrients, such as manganese, on plants is well known. Yet the high content of mobile forms of manganese in the soil often causes complete loss of the harvest. This content may reach dangerous levels if large amounts of organic fertilizers are incorporated into unlimed acid soils with a high manganese content.

Chapter 1

History of Agricultural Chemistry. Chemicalization of Agriculture in the USSR

1.1 Historical Review of Agrochemical Science

The knowledge how to improve the fertility of soils with the aid of various fertilizer materials has been accumulated by generations of farmers toiling in fields. Manuring of soil and incorporation into the latter of all kinds of farm waste to enhance the yield of crops have been practised for millennia. Way back in ancient Rome, green manure was used (vegetable matter ploughed down to enrich the soil in Egypt), and the fertilizing effect of ash, lime (marl), and gypsum was a matter of common knowledge. However, nothing was known about what made these things work, and it took centuries of arduous efforts to shed the veil of mystery that shrouded plant nutrition.

Proceeding from purely speculative premises, materialist philosophers of ancient Greece stated that fire, earth, water, and air are the elements necessary for plant life. They were not far from the truth since the sun (fire) is indeed a source of light and energy for photosynthesis in plants, earth (soil) supplies inorganic nutrients, air is a source of carbon dioxide, and water is not merely a major component of green plants, constituting three quarters of their mass, but also a predominant factor involved in all basic processes occurring in living plants.

Ancient scholars set forth the concept of "fat" of the land, on which soil fertility was dependent. This concept was elaborated later in the humus theory of plant nutrition.

Rather clearly defined ideas as regards the role of nutrients and the importance of fertilizers were expressed as far back as 1563 by the French naturalist Palissy who wrote that salts form the basis of life and growth of all crops and that manure taken to fields would be of no significance if

it did not contain the salts remaining after decomposition of hay and straw.

It took another century for the German chemist Glauber (1656) to prove in his experiments that addition of saltpetre to soil markedly increases the yield of crops. However, his contemporaries could not appreciate this finding because nitrogen was yet to be discovered after more than a hundred years, and its role in the life of plants was elucidated even much later.

Original ideas concerning aerial nutrition of plants were set forth by M. V. Lomonosov in 1753: "The profuse growth of luxuriant trees that have taken root in barren sand is a clear manifestation that their succulent leaves receive copious nourishment from air."

That aerial and root nutritions are closely associated was pointed out by Lavoisier who in 1775 discovered nitrogen in the atmosphere. He wrote: "Plants take up substances necessary for their organization from the surrounding air, from water, and, generally speaking, from the mineral kingdom".

Practical needs of agriculture gave rise to the early theories of inorganic nutrition of plants via roots.

In his book *On Agriculture* treating at length the importance of individual crops, Komov (1750-1792) wrote about the necessity to fertilize "bad" soils, emphasizing the importance of manure not only as a fertilizer, but also as an agent enabling conservation of moisture in the soil and improving its structure. Komov also pointed out the importance of lime as a means for increasing yields of farm crops.

These speculations have a lot in common with the ideas of Bolotov (1738-1833) who remarked in his paper "On Manure Salts" that the nutrients available to plants emerge from organic fertilizers.

The role of "alkali-salt substances", that is, inorganic nutrients, in plant nutrition was outlined by Poshman (1792-1852) in his book *A Manual for Preparation of Dry and Wet Fertilizers to Be Used on Arable Lands.*

Pavlov (1794-1840) believed that to fertilize a soil means to enrich it, to improve its physical properties, and to neutralize its acidity or promote decomposition of the organic matter present there.

Insofar as inorganic nutrition is concerned, interesting views were expressed in 1789 by Rückert who suggested that every plant thrives on a soil with a composition optimal for its species and that certain plants cultivated several years in a row on the same field deplete its fertility considerably. He believed that such depletion can be forestalled by using a fertilizer in which the deficient nutrient is predominant.

By the end of the 18th century, the humus theory set forth in 1761 by the Swedish chemist Valerius had been universally accepted in Western Europe. The correct proposition that the humus is of crucial importance for soil fertility was offset in this theory by the wrong statement that the humus is the only substance in the soil that can serve for nutrition of plants.

Since the importance of inorganic ash salts for plant nutrition was hard to refute even at that time, Valerius contended that they promote dissolution of the humus (which, in his misconception, was directly assimilated through roots).

The year 1836 marks the beginning of studies, following the work by the French scientist Boussingault, into the cycle of nutrients in agriculture and the discovery that nitrogen is accumulated in the soil by leguminous crops. In place of the humus theory, Boussingault proposed the nitrogen theory of nutrition, pointed out the primary role of nitrogen in agriculture, and demonstrated that the introduction of clover (or other legumes) into crop rotation improves the nitrogen balance and leads to substantial increases in crop yields. He suggested that legumes take up nitrogen from air. At the same time, his work provided evidence that the amount of carbon in the crop has nothing to do with its content in manure, the source of carbon for plants being atmospheric carbon dioxide.

A turning point in plant nutrition research was publication in 1840 of the book *Organic Chemistry in Its Application to Agriculture and Physiology* by the German scientist Justus von Liebig, in which the humus theory was severely criticized and the theory of inorganic nutrition of plants was advocated. Liebig explained the factors responsible for impoverishment of soil and set forth a theory of soil fer-

tilization, based on the concept of full return of all the nutrients taken up by plants back into the soil.

Later, Timiryazev remarked that the theory of full return was one of the greatest achievements of science.

Having shown that the depletion of various nutrients in the soil is irregular, Liebig formulated the "law of minimum", which states that the crop size depends on the amount of the minimum (i.e. the most deficient) factor. For example, if nitrogen or zinc is deficient in the cultivation of maize, no matter how much phosphorus, potassium, and other nutrients are added, they will not increase the crop yield.

Karl Marx wrote: "To have developed, from the point of view of natural science, the negative, i.e. distractive side of modern agriculture, is one of Liebig's immortal merits".

Liebig attracted widespread attention to different aspects of the cycle and balance of inorganic nutrients.

Today, these problems remain topical from the standpoint of both agricultural chemistry and environmental control.

Liebig's work has been of great benefit, yet, some of his ideas were erroneous. For example, he believed that plants receive enough nitrogen with precipitations. He explained the enrichment of the soil with nitrogen by leguminous plants by that they take up increasingly greater amounts of ammonia from the atmosphere over the long period of their growth, as well as more nitrogen with precipitations.

Liebig's opinion that ash nutrients are important, while there is no need to worry about nitrogen, was undermined by centuries of manuring experience.

Of great importance for evolution of the inorganic nutrition theory were experiments in which plants were grown on sterile media (water or sand) with the necessary nutrients being supplied in the form of mineral salts. In 1858, Knop and Sachs succeeded in bringing plants grown on artificial nutrient media with a supply of mineral salts to full maturity.

Hellriegel's experiments (1886) with legumes revealed that these crops are capable of taking up molecular nitrogen from air with the aid of the nodule bacteria living on their roots.

Experiments with plants grown on nutrient mixtures of mineral salts have proven that plants need nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, and, subsequently, certain micronutrients, as well as shown the equivalence and indispensability of each inorganic nutrient for plants.

Research into plant nutrition was paralleled by application of inorganic fertilizers in agriculture. By the mid 19th century, two inorganic fertilizers had been adopted for practical use in agriculture, i.e. Chile saltpetre and superphosphate. In 1865, potassium salts started being mined in the vicinity of Stassfurt.

In Russia, systematic research into plant nutrition and application of fertilizers dates back to the sixties and seventies of the past century. Of particular importance were the experiments carried out by Engelgardt, Mendeleev, Kostychev, and Timiryazev.

Professor A. N. Engelgardt (1832-1893), a prominent democrat of his time and author of *Letters from the Country* and *The Basic Chemistry of Agriculture*, was an ardent proponent of fertilizers. Engelgardt supervised application of phosphorus fertilizers in the form of ground phosphate rock. He attached a great deal of importance to green manure. He pointed out that ground phosphate rock and green manure are indispensable for reclaiming vast tracts of land in the north. Engelgardt was also a staunch advocate of liming and application of inorganic fertilizers in combination with organic ones.

Mendeleev (1834-1907) was actively involved in agriculture. He set up field stations for studying the effect of fertilizers. While appearing publicly in favour of laying the base of agricultural chemistry in his country, Mendeleev thought it necessary to experiment with synthetic fertilizers. At the same time, Mendeleev was in support of an overall approach to enhancing productivity in agriculture. He wrote: "I rebel against those who preach, in print or by word of mouth, that all it takes is fertilizers; that once a field has been properly fertilized, it can be ploughed somehow or other."

Mendeleev conducted the first field experiments aimed at improving the effectiveness of fertilizers in different parts

of the country; that is, the basic principles of the Geographical Network of Field Experiments were set forth to trace the pattern of fertilizer efficiency according to soil and climatic zones.

In 1884, Kostychev, one of the founders of Russian agronomy, published his book *The Science of Fertilizers* in which he criticized the "full return" theory proposed by Liebig. Kostychev noted that the fertility of the soil depends not only on the amount of nutrients it contains, but also on its structure and other physical properties. He established a direct link between soil structure and humus accumulation. His work includes a definition of the phosphate status in soils.

In his book *Twenty Lectures on Agricultural Chemistry*, Gustavson (1842-1901) covered different aspects of soil and fertilizer chemistry, analysis of soils, fertilizers, and fodders.

The basic theory of agrochemistry owes a lot to the classic research of Timiryazev (1843-1920) who introduced greenhouse experiments into scientific practice.

Timiryazev held experimental work in high esteem. In 1872, he built the first greenhouse in Russia.

The tasks formulated by Timiryazev for agriculture are fully applicable to modern agrochemistry as well. He saw the fundamental task of agricultural science in studying the specific procedures of growing farm crops and taking careful account of the requirements of cultivated plants to the environmental conditions. Timiryazev had an exceptional gift of putting the most complicated scientific phenomena in lucid terms. Being deeply involved in the theoretical aspects of plant physiology and carrying out research on assimilation in a field bordering physics, Timiryazev was nonetheless greatly interested in agriculture and always emphasized the close relationship between agricultural chemistry and plant physiology.

Timiryazev waged an unrelenting battle against the narrow-minded practicism standing in the way of intensive research.

Progress in Soviet agrochemistry is inexorably connected with the research activities of Pryanishnikov (1865-1948).

The scope of Pryanishnikov's scientific interests was amazingly broad. He supervised research into phosphorus

nutrition of plants, more particularly assimilation of phosphorus by plants from phosphorites and application of ground phosphate rock as a fertilizer.

In connection with the development of potassium mines in Solikamsk, Pryanishnikov and his pupils carried out a series of experiments involving the uptake of potassic salts by plants. He always paid much attention to studying the role of biological nitrogen in agriculture and emphasized the need to use organic fertilizers. Pryanishnikov initiated research to elucidate the effect of micronutrients on plants.

Pryanishnikov proved that ammonium salts are equivalent to nitrates as sources of nitrogen nutrition of plants. He defined the conditions under which the supply of ammonium salts to plants does not bring about undesirable aftereffects. The importance of this work cannot be overrated for it has paved the way to application of ammonium salts as nitrogen fertilizers.

Pryanishnikov began to study the conversion of nitrogen nutrients in plants with the degradation of proteinaceous substances and the subsequent transformations of the degradation products. It was known at that time that the germination of seeds rich in proteinaceous substances yields large amounts of asparagine. Pryanishnikov demonstrated that degrading proteins form amino acids from which ammonia is eliminated in a subsequent step. The ammonia resulting from germination of seeds is bound as asparagine and is thus passed into a non-toxic compound, whereas asparagine may be reutilized in plants in biosynthetic processes. Pryanishnikov referred to asparagine as "neutralized ammonia". These experiments are indicative of a close relationship between nitrogen and carbohydrate metabolisms. Investigations of ammonium nitrate, a salt in which ammonia and nitrate are combined, have led Pryanishnikov to call it "fertilizer of the future".

The classic studies undertaken by Pryanishnikov into nitrogen metabolism and plant nutrition were of greatest importance for resolving the practical problems involved in application of fertilizers and, at a later stage, for the development of the nitrogen fertilizer industry in this country.

Pryanishnikov edited 17 volumes of collected papers under the general title *From the Results of Greenhouse Experiments and Laboratory Work*. He took an active part in setting up the Scientific Institute of Fertilizers at the USSR Council of National Economy, the USSR Research Institute of Fertilizers, Agrotechnics, and Agronomical Soil Science, and the Central Scientific Research Institute of Sugar Industry. The fundamental works written by Pryanishnikov, including *Agricultural Chemistry* and *Nitrogen in the Life of Plants and in Soviet Agriculture*, have been used until recently as textbooks in the USSR and other countries.

The creative scientific activities of Pryanishnikov and the Soviet school of agrochemists established by him have been the major factors of development of agrochemistry in the Soviet Union on broad physiological and biochemical bases with due account for the practical aspects of chemicalization of agriculture.

Many other scientists have made sizable contributions to the development of Soviet agrochemistry.

Kossovich (1862-1915) demonstrated the possibility of assimilation of ammonia nitrogen by plants without its conversion into the nitrate form. He proved that nodule bacteria bind the atmospheric nitrogen arriving via roots rather than leaves of leguminous plants. His other studies involve assimilation of air nitrogen by free-living bacteria. Kossovich also examined the active role of root exudates in passing phosphorus from phosphorite into solution.

Gedroits (1872-1932) offered a classification of absorbing capacity of the soil and discovered that the exchange phenomena occurring in it involve humus, organic residues, minerals, and microorganisms. Gedroits' work was instrumental in determining the potential acidity of the soil and provided the basic theory of liming and gypsuming of soils. He also found that all soils are capable of exchanging the absorbed cations (both metals and hydrogen) present in their absorbing complex, the number of cations absorbed by the soil being equal to that of the cations displaced from the soil solution. It was established that the cation-exchange reactions are instantaneous.

Lebedyantsev (1878-1941) was the first to find it possible to effectively use ground phosphate rock in the northern

part of the Black Earth zone. He carried out comparative analysis of effectiveness of inorganic fertilizers in various parts of the Soviet Union.

Kedrov-Zikhman (1885-1964) developed the basic theory of liming. He also studied the effect of magnesium and boron on plants.

Naidin (1893-1969) proposed to set up and then headed the USSR Geographical Network of Experiments with Fertilizers. He has written more than 150 scientific and popular science books and papers dealing with application of fertilizers in various parts of our country, fertilizer systems for crop rotations, and other subjects.

Sabinin (1889-1951) conducted research on inorganic nutrition and other aspects of plant physiology. His monograph *Inorganic Nutrition of Plants*, published in 1940, was awarded the Timiryazev Prize. Sabinin supervised investigations of the metabolic processes in root systems. He also studied the water regime of plant cells and tissues, the structure of the protoplast, photosynthesis and its relation to inorganic nutrition of plants.

Dikusar (1897-1973) is known for his many works on nitrogen nutrition of plants, the role of nitrogen and phosphorus in metabolism, and conditions of ammonia and nitrate nutrition of plants.

Katalymov (1907-1969) was involved with the theory and practices of using micronutrients in agriculture.

Turchin (1902-1965) carried out agrochemical assessment of various forms of simple and compound inorganic fertilizers. Having pioneered the use of compounds labelled with the stable nitrogen isotope ^{15}N, he conducted classic research to elucidate the pathways of the nitrates, ammonium, and amides entering plants and utilized in the synthesis of amino acids and proteins. These studies outlined the sequence of formation of amino acids in plants and established the fact of continuous turnover of proteins. Turchin investigated the processes of biological fixation of nitrogen as well.

Klechkovsky (1900-1972) explored phosphate nutrition of plants, the quantitative aspects of fertilizer activity, and optimal nutrient ratios. Klechkovsky was one of the founders of the agrochemistry of man-made radionuclides.

One of the ways to reduce the content of radionuclides in agricultural produce is application of inorganic and organic fertilizers.

Peive (1906-1972) has developed the theory of discriminatory application of micronutrient fertilizers in Soviet plant growing taking into account the content of available micronutrients in soils and the physiological aspects of plants. Peive has made a valuable contribution to the theory concerning the effect of trace metals on enzymes and enzyme systems. His other activities include studies into the agrochemistry of potassium, aluminium, calcium, and phosphorus, elaboration of new methods for determining mobile forms of micronutrients in soils, as well as studies of their content and distribution pattern in the latter. Peive attached a great deal of importance to elucidating the role of micronutrients in the symbiotic fixation of molecular nitrogen from air.

Avdonin (1903-1980) investigated plant nutrition at different stages of growth and laid the theoretical base of crop dressing. Other areas of his research included enhancement of the fertility of soddy podsolic soils, techniques to improve their properties and to increase the effectiveness of the inorganic fertilizers incorporated into them. He supervised investigations as regards winter hardiness of cereals and perennial grasses in the Non-Black Earth zone and also the effect of soils and fertilizers on crop quality.

Sokolov (1898-1980) coordinated the research efforts aimed at providing an agrochemical classification of soils in the Soviet Union as well as defining their fertilizer requirements.

He has developed a method for determining the exchange acidity of soils and procedures to identify forms of soil phosphates and to find the content of phosphorus compounds in plants.

Sokolov evaluated the importance of rock phosphatization and examined the nature of phosphorus fixation in soils. He also invented a process for producing granulated superphosphate. Much of his research was focussed on phosphorus metabolism in plants, optimal conditions of plant nutrition, and the dynamics of soil processes. His other accomplishments include a radiobiological method for determining the

true factor of phosphorus utilization by plants and original works in plant physiology, agrochemistry, and pedology.

Volfkovich (1896-1980) is a co-inventor of the process for converting raw apatite into superphosphate. He experimented with extraction of phosphoric acid from domestic rock phosphate.

Volfkovich supervised research into the chemistry and processing of inorganic fertilizers. Together with Pryanishnikov, he made a great contribution to planning and implementation of chemicalization of Soviet agriculture.

1.2 Fertilizers: A Major Factor of High Yields

The difference between the intake of nutrients into the soil and their removal from the latter constitutes the nutrient balance.

The removal of nutrients from the soil is determined by their amount taken up by primary and secondary crops from unit arable area. The return of nutrients into the soil is determined by their compensating amount brought back with fertilizers, seeds, and root residues, by the process of molecular nitrogen fixation, and from other possible sources.

Farm crops are characterized by different nutritive requirements and different removal of nutrients from the soil during harvesting. To harvest about 30 metric centners of wheat from a hectare requires 110 kg N, 40 kg P_2O_5, and 70 kg K_2O. Harvesting of 300 centners of potato from a hectare removes 150 kg N, 60 kg P_2O_5, and 270 kg K_2O. Cultivation without application of fertilizers impoverishes the soil, and crop yields diminish from year to year. As is stated in the "Guidelines of Economic and Social Development of the USSR for 1981-1985 and for the Period Ending in 1990", the chief task of the agro-industrial complex is to ensure reliable supply of foodstuffs and agricultural raw materials. Accomplishment of this task is possible only through further increases in yield and productivity per hectare of arable land.

The yield of crops and its increase are determined by the combined effect of the following major factors of growth: light, heat, moisture, and nutrition.

However, even under conditions of industrialized agriculture, the possibility of controlling these factors to promote the growth of crops and increase their yields varies widely from one place to another. Fertilizers and, in broader terms, extensive chemicalization of agriculture are to play a predominant role in increasing the yield of farm crops.

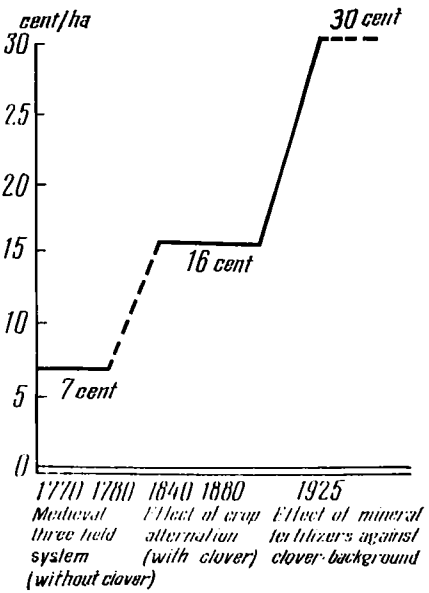


Fig. 1.1: Changes in wheat yields in western Europe over a period of 150 years

The worldwide experience provides convincing evidence to the effect that crop yields are directly dependent on the amounts of applied fertilizers (Fig. 1.1). The relationship between yields and application of fertilizers is clearly seen from the listing of different countries (Table 1.1).

At present, every fourth person living on this planet consumes alimentary products resulting from yield increase due to fertilizers. According to the statistics of the Food and Agriculture Organization of the UN (FAO), if the Earth's population approaches the six billion mark by the year 2000, to ensure adequate supply of food worldwide the

Table 1.1. Application of Fertilizers and Yields of Wheat and Potato in Different Countries (1977)

Country	NPK (kg/ha)	Yield (cent/ha)	
		wheat	potato
Netherlands	758	52	338
Japan	430	62	190
FRG	423	45	284
GDR	353	43	275
Great Britain	274	49	284
Czechoslovakia	320	43	161
France	269	42	275
Italy	105	23	185
USA	106	24	292
Spain	82	15	147
USSR	73	15	118
India	20	14	115

yield of grain crops must increase by 100 per cent and that of animal products by 200 per cent.

As predicted by FAO, the world demand in fertilizers by the year 2000 will amount to 307.2 million tons of nutrients, including 170 million tons of nitrogen, 70 million tons of P_2O_5, and 60 million tons of K_2O. The application of fertilizers per capita will increase from 55 to 145 kg of nutrients in industrially developed countries and from 7 to 23 kg in developing countries. Thus, within the next twenty years, the production of fertilizers worldwide must increase approximately three-fold.

Specialists have calculated that half of the estimated yield increase is due to fertilizers, while the other half is ensured by other means, such as farming practices, breeding, land reclamation, and so on. Reports of American research institutions indicate that 41 per cent of the post-war yield increase in the United States were due to fertilizers, 15 to 20 per cent due to herbicides and other plant protection chemicals, 15 per cent due to improved farming practices, 8 per cent due to hybrid seeds, 5 per cent due to irrigation, and 11 to 18 per cent due to other factors.

As yields increase, crops take up more nutrients, therefore, the higher the conventional yield of any crop, the

greater the amount of fertilizers used. It should be borne in mind, however, that yields increase with fertilizer application rates only up to a certain point at which a balance is reached between the cost per fertilizer unit and the return per yield unit.

The production of fertilizers involves considerable power consumption. For example, there are about 600 plants all over the world currently synthesizing NH_3. The power consumed by these plants daily is equivalent to 125 million

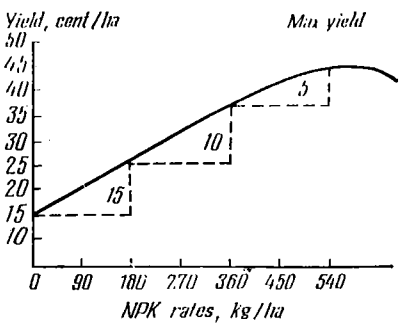


Fig. 1.2: Yields versus fertilizer rate

litres of oil. Therefore, increasing fertilizer application rates is economically justified to a point where the expenditures involved in the use of additional quantities of fertilizers are fully compensated by the return from the crop yield (Fig. 1.2).

Thus, the main task of chemicalization of agriculture in this country is to ensure maximum return from the available fertilizer resources.

Application of fertilizers must go hand in hand with advanced farming practices (Table 1.2).

Fertilizer application times and methods (Table 1.3) are of great importance in their rational use.

The effectiveness of inorganic fertilizers is substantially enhanced by irrigation or sufficient amounts of precipitations (Fig. 1.3).

Application of fertilizers also improves the crop quality. Numerous experiments in various soil and climatic zones of the Soviet Union have determined the effect of rates and

Table 1.2. Effect of Various Agronomical Practices on Potato Yield (sandy soils)

Procedure	Yield, cent/ha	Increment, cent/ha
No fertilizers, late planting, small tubers, insufficient attendance	91	—
Application of fertilizers	160	69
Advanced farming practices, without fertilizers	154	63
Advanced farming practices and fertilizers	274	183

Table 1.3. Sugar Beet Yield Increments (in centres per hectare) Depending on Fertilizer Application Times and Methods

Field station	Application of NPK	
	in spring, incorporation by cultivator	in autumn, plough-down
Kharkov	27	65
Mironovka	26	50
Kursk	37	60

forms of nitrogen fertilizers on changes in grain quality, particularly the protein content in winter wheat kernels.

Speaking about the rapid advances in chemicalization of agriculture, mention should be made of the importance of organic fertilizers, supported by centuries of their use. The steadily increasing use of inorganic fertilizers leads to higher yields, which, in turn, permits expanding the cattle stock, hence, making manure more readily available.

Pryanishnikov believed that to underrate manure means to misuse the nutrients present in inorganic fertilizers. Organic fertilizers, primarily manure, belong to the basic components of a properly formulated fertilizer system.

According to reports of research centres, 20 to 30 tons of manure applied per hectare of arable land in the Non-Black Earth zone increase the yield of grain crops by 6 to 7 cent-

ners, the corresponding increments for potatoes, root crops, and ensilage crops being 60 to 70, up to 150, and 150 to 200 centners per hectare, respectively. The aftereffect of manure lasts four to five years, each ton of manure accounting for a yield increment of one centner (in terms of grain) over this period.

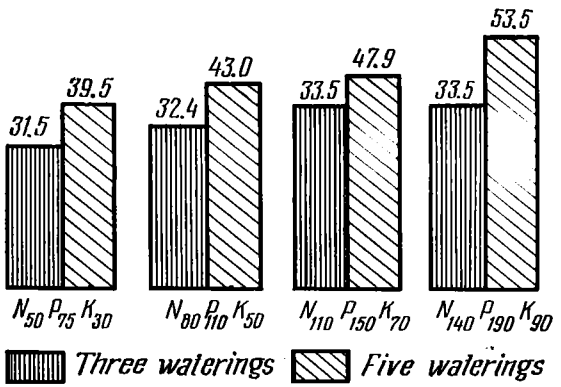


Fig. 1.3: Effect of fertilizer rates on spring wheat yields, depending on the number of waterings

For example, in the experiments carried out at the Dolgoprudny field station, 36 tons of manure increased the yield of four rotating crops by a total of 34 centners in terms of grain (Table 1.4).

Table 1.4. Yield Increments in Crop Rotation Due to Application of 36 Tons of Manure (averaged over a 15-year period)

Crop	Absolute increment, cent/ha	In terms of grain, centners
Rye (grain)	10.7	10.7
Oat (grain)	5.3	5.3
Clover (hay)	6.5	2.6
Fodder beet (roots)	155.6	15.5
Total		34.1

1.3 Economical Effectiveness of Fertilizers and Their Production Rates in the USSR

Chemicalization of agriculture is a basic factor of increasing yields of farm crops, improving their quality, and enhancing soil fertility.

Application of fertilizers is profitable from the economic standpoint. A case in point is the effectiveness of inorganic fertilizers applied to raise grain crops yields (Table 1.5).

Table 1.5. Economical Effectiveness of Inorganic Fertilizers Applied in the USSR to Raise Grain Crop Yields (averaged over the 1969-1970 period)

Crop	Number of experiments	Applied per hectare, kg			Yield from fertilized soils, cent/ha	Increment due to fertilizers, cent/ha	Crop-to-active ingredient ratio	Net return, rubles	
		N	P_2O_5	K_2O				per ha	per ruble of expenditures
Winter rye	82	60	60	50	19.0	5.7	3.4	35.09	1.00
Winter wheat	383	55	55	45	32.4	7.0	4.5	31.02	0.96
Spring wheat	323	45	50	40	22.0	5.1	3.8	26.69	1.15
Oat	84	45	40	50	21.0	3.0	4.4	33.61	1.28
Barley	346	55	50	50	25.2	6.1	3.9	27.13	0.85

Calculations show that one ruble spent on inorganic fertilizers returns 2.3 rubles worth of crops, and 1 kg of the active ingredient returns 5 to 10 kg of grain or an equivalent amount of other produce. The net earnings from application of fertilizers equal an average of 3.4 billion rubles per annum. The expenditures involved in the purchase and application of inorganic fertilizers throughout the country constitute anywhere from 15 to 17 per cent of the total amount of money spent on cultivation of crops.

The return from fertilizers depends on the natural fertility of the soil. For example, in the Non-Black Earth zone where soils are characterized by high moisture content and low natural fertility, fertilizers account for 70 to 80

per cent of the increase in crop yields amounting to 30 and more centners. Only half of the yield increment is due to fertilizers in dry steppes, where an important role is played by the tillage system and accumulation of moisture, drought resistance of the cultivated varieties, and other factors.

The production and application of inorganic fertilizers in the USSR keep abreast of the steadily increasing industrial potential, their rates being well above those in other countries (Tables 1.6 and 1.7).

Table 1.6. Increasing Production of Inorganic Fertilizers in the USSR (in thousands of tons of active ingredients)

Year	Total nutrients	Including			N : P_2O_5 : K_2O
		N	P_2O_5	K_2O	
1928	25.6	2.3	23.3	—	1 : 10 : 0
1935	50.5	76.4	311.6	121.6	1 : 4 : 1.6
1940	746.0	199.0	326.0	221.0	1 : 1.6 : 1.1
1945	253.0	152.6	46.0	54.6	1 : 0.3 : 0.4
1950	1235.7	392.2	531.0	312.0	1 : 1.4 : 0.8
1955	2299.4	613.0	895.0	791.0	1 : 1.5 : 1.3
1960	3280.5	1003.0	1191.7	1084.0	1 : 1.2 : 1.1
1965	7389.0	2722.0	2300.0	2368.0	1 : 0.8 : 0.9
1970	13080.0	5422.0	3566.0	4092.0	1 : 0.7 : 0.8
1975	22122.0	8036.0	5703.0	8383.0	1 : 0.7 : 1.0
1980	24800.0				

In 1973, the Soviet Union became the world's leading country in fertilizer production. In 1975, 90.2 million tons of inorganic fertilizers were produced. Five years later, the total output of fertilizers reached 104 million tons or, in terms of 100% nutrients, 24.8 million tons.

In 1980, Soviet farms were supplied 18.8 million tons of inorganic fertilizers, including 8.3 million tons of N, 4.6 million tons of P_2O_5, and 4.9 million tons of K_2O.

The estimated output for 1985 will be a total of 150 to 155 million tons or, in terms of 100% nutrients, 36 to 37 million tons. In 1985 farms will receive a total of 115 million tons of fertilizers or, in terms of 100% nutrients, 26.7 million tons.

Table 1.7. Increasing Use of Inorganic Fertilizers in the USSR

Crops	Years	Application rate (kg nutrients per ha)	Crops	Years	Application rate (kg nutrients per ha)
Grain crops	1966-1970	22	Sugar beet	1966-1970	230
	1971-1975	38		1971-1975	306
	1976-1980	51		1976-1980	460
Cotton	1966-1970	325	Potato	1966-1970	142
	1971-1975	364		1971-1975	221
	1976-1980	409		1976-1980	272
Fibre flax	1966-1970	138	Vegetables and melons	1966-1970	113
	1971-1975	172		1971-1975	189
	1976-1980	201		1976-1980	269

1.4 Chemicalization of Agriculture: A Decisive Factor of Raising the Level of Agricultural Production

At present, agriculture in this country is undergoing intensification on the basis of extensive chemicalization, mechanization, land reclamation, specialization and concentration of production. Economic cooperation of agricultural enterprises and agro-industrial integration are under way.

The Communist Party has proposed an overall integrated program of agricultural development, which will permit the output of farm products to be substantially increased.

The specialization and intensification of agricultural production are aimed at increasing the productivity of farming and animal husbandry, bringing forward new tasks in application of fertilizers.

A prerequisite for successful fulfillment of the specialization and intensification program is putting the technology of crop cultivation on an industrial basis.

The chemicalization program is based on intensive development of agricultural chemistry, which has become possible owing to advances in many biological disciplines and methodology.

Agricultural production is embarking upon advanced fertilizer application techniques, including local application of inorganic fertilizers (preseeding, starter, and root treatments) ensuring higher return, especially in such areas as the Volga Lands, Siberia, and North Kazakhstan. Next in importance after chemicalization and land reclamation comes improvement of the physical properties of the soil, determined primarily by the quality and quantity of humus. The inability to control the hydrophysical properties of the soil imposes a limitation on yield increase.

A lot has been done to elucidate the transformation of soil-derived nitrogen, the effect of the fertilizer nitrogen on the latter, the complex processes of mobilization and immobilization of nitrogen from various forms of fertilizers in the soil, and the nitrogen utilization factor of fertilizers and the soil.

Obtaining high yields of top-quality crops may be restricted by micronutrient deficiency, which is why the need arises to apply not only macro- but also micronutrient fertilizers. Application of micronutrient fertilizers may also be necessitated by such factors as the desire to increase yields by incorporating greater amounts of fertilizers in cultivation of heavy-producing varieties, as well as liming of acid soils, reclamation of peat bogs, and irrigation in drought-affected regions.

When it comes to realization of the intensive chemicalization program, one of the major agrochemical problems is to balance out plant nutrition by all necessary nutrients, including micronutrients.

Balanced nutrition of plants, based on increasingly refined recommendations by research institutions, makes it possible to drastically improve the fertilizer utilization factors.

In some cases, overfertilization or application of fertilizers with upset nutrient balance leads to poor crop quality and pollution of the environment (soil, water, air). Imprudent use of fertilizers may do a lot of harm, and scientists are actively searching for ways to enhance the effectiveness and utilization factor of fertilizers and to minimize their losses.

The return from fertilizers can be substantially increased

also by developing new fertilizer formulations and improved methods of their application in combination with chemical ameliorants and plant protectants.

It is important to program yields with due account for such factors as the soil, variety, fertilizers, and the bioclimatic potential with recourse to a particular system of farming and an increase in labour efficiency as a result of extensive implementation of industrial technology of crop cultivation.

In 1980, grain maize was cultivated on an industrial basis over a total area of 1.2 million hectares, sunflower over an area of 0.6 million hectares, and soybean on 0.2 million hectares. There are intentions to substantially extend the areas of industrialized crop cultivation: to 100 per cent for grain maize, sunflower, soybean, rice, and sugar beet and to at least 30-40 per cent for potatoes, tomatoes, onions, cotton, and fibre flax.

It should be pointed out, however, that, if the agrotechnical factors of yield programming can be controlled, such factors as water and, particularly, light and heat are virtually beyond control under field conditions or controllable over a limited area. Therefore, yields, especially increased ones, can be programmed only under favourable weather conditions and guaranteed only in the case of irrigation and hothouse farming.

Fertilizer application rates for programmed yields are determined either by way of calculation or from the results of field experiments, or both. Calculations are made using the nutrient balance, yield increment, and rate balance methods.

The nutrient balance method is based on removal of nutrients per 10 centners of the main product, also taking into account the by-products, the factors of utilization of soil-derived nutrients, fertilizers, and nitrogen derived from the afterharvesting and root residues of leguminous crops.

In the yield increment method, the removal of nutrients is calculated in relation to the yield increment. The yield without fertilizers is taken from field data or calculated from the content of mobile phosphorus in the soil, which appears in the second or first minimum among other nu-

trients. The calculated rate is then corrected depending on the nutrient content in the soil.

Calculations using the rate balance method are based on removal of nutrients per 10 centners of the main product, rated nutrient balance per crop rotation, distribution coefficients of primary nutrients and the nitrogen derived from the afterharvesting and root residues of legumes.

Each of the above methods permits calculation of the fertilizer rates ensuring conventional yields.

Formulation of a fertilizer system for short-term (or continuous) crop rotation constitutes the highest level of scientifically substantiated application of fertilizers, as opposed to determination of fertilizer rates for individual crops on a yearly basis. Based on an estimated nutrient balance in the soil, the fertilizer system allows obtaining a conventional yield while maintaining and even increasing soil fertility, equalizing it over the entire arable area, using fertilizers more effectively, and minimizing the possibility of environmental pollution. It should be emphasized that, no matter which method is used for calculating the fertilizer rate in crop rotation, the formulated fertilizer system should always be ajusted in accordance with the actual nutrient balance per rotation cycle.

Development of ways to effectively use fertilizers in agriculture is the chief task of agrochemistry.

1.5 Agrochemical Service in the USSR

Rational use of inorganic and organic fertilizers as well as chemical ameliorants (lime and gypsum) and plant protectants is to a great extent dependent on the availability of an agrochemical service in agriculture. Consequently, an integrated agrochemical service has been created in the Soviet Union.

The management of the national agrochemical service is exercised by the USSR Ministry of Agriculture through the agency of the USSR Production and Research Association "Soyuzselkhozkhimiya", while the research and methodological activities are supervised by the Central Institute of Agrochemical Service (TsINAO) and its affiliates located in the major natural and climatic zones of the Soviet Union.

In the Soviet Republics, the management of the agrochemical service rests with the republican Ministries of Agriculture acting through their respective production and research associations "Selkhozkhimiya". In the Autonomous Soviet Socialist Republics, territories (krays), regions (oblasts), and districts, local production associations "Selkhozkhimiya" have been set up with republican (ASSR), territorial, zonal, and district agrochemical laboratories, planning and surveying stations of chemicalization, and plant protection stations. Under the direct auspices of collective and state farms are farm (interfarm) chemicalization stations with agrochemical laboratories.

TsINAO with its network of affiliates and in cooperation with the Central Experimental Research, Planning, and Technological Laboratory of Chemicalization of Agriculture (TsELKHIM) prepare recommendations for rational distribution of the fertilizer resources in the country, rational use of fertilizers and fodders at farms, and rational fertilizer application techniques.

The association "Soyuzselkhozkhimiya" is responsible for scientifically substantiated use of inorganic and organic fertilizers, chemical and biological plant protectants, soil ameliorants, food additives, growth stimulators, and other chemicals.

The association makes forecasts concerning the needs of farms in chemicals and prepares summaries of the requests issued by agricultural enterprises for any chemical. Among the various undertakings of the association are extraction of peat, local calcareous and gypsiferous materials, as well as carrying out of all chemicalization procedures at farms, including keeping all the necessary records to ensure effective use of the chemicals. The association must take timely measures to control pests, plant diseases, and weeds and make sure that the pesticides and chemicals are employed in a prescribed manner.

The republican, territorial, regional, and zonal agrochemical laboratories or planning and surveying stations of chemicalization comprise the following departments: operations, analysis and assaying, chemicalization of animal husbandry, analysis of fodders and plants, environmental control, management and planning.

The operational department includes groups involved in agrochemical testing of soils, writing recommendations and project estimates for use of fertilizers, and mapping.

The analytical department is manned by soil and fertilizer analyzers and assayers.

The department of chemicalization of animal husbandry has groups trained to take samples and write recommendations, as well as to analyze fodders and plants.

The environmental control department has groups of chemical toxicology and radiology.

The regional and zonal agrochemical laboratories are currently being reorganized into planning and surveying stations of chemicalization and report, to the republican agrochemical laboratory whose main tasks are as follows: supervision of agrochemical soil testing to make sure that high standards are maintained and summarizing the test results; supervision of field experiments and summarizing their results; estimating the quality of fodders and locally available fertilizers and writing appropriate recommendations; assistance in equipping agrochemical laboratories and supervision of use of the equipment; implementation of up-to-date routine analysis techniques; investigation of the nutrient balance in the different soils of the republic; introduction of advanced practices and dissemination of agrochemical knowledge; monitoring the activities of agrochemical laboratories; and methodological guidance of the research carried out in the laboratories.

The primary tasks to be accomplished by regional and zonal laboratories include: agrochemical examination of soils; routine analyses of soils, plants, and fertilizers; field experiments with fertilizers; determination of the quality of fodders and local fertilizers; incoming quality control of the supplied fertilizers; supervision of their storage and application; writing project estimates and recommendations for chemicalization; drawing agrochemical charts for farms; evaluation of the needs of individual farms in fertilizers; studying the nutrient balance in various soils; monitoring environmental pollution; advanced training of farm specialists and propaganda of progressive experience.

A single planning and surveying station of chemicalization serves an average of 2.7 million hectares of farmland

(including 1.1 million hectares of arable land) or about 250 farms. The soils of collective and state farms are examined agrochemically once in four or five years. The examination results are used to draw charts indicating soil acidity and the contents of mobile phosphorus and potassium. The charts are accompanied by reports including analysis data and recommendations for rational use of fertilizers.

Determined in the vegetable matter are nitrogen, phosphorus, potassium, calcium, sodium, protein, raw gelatin, starch, sugar, ascorbic acid, fats, and some substances specific of certain crops (tea, tobacco, oil-bearing crops). Analysis of fodders additionally includes determination of cellulose, carotene, organic acids, and micronutrients with subsequent classification, or grading, of the fodders.

The results of field experiments with fertilizers are submitted by the planning and surveying stations of chemicalization, in the form of report cards, to the computer center of TsINAO for processing and printing out of summaries. For soil and plant analyses to proceed on a continuous basis, the laboratories are equipped with high-performance state-of-the-art hardware. At present, an automatic control system designed specifically for chemicalization of agriculture (ASUagrokhim) is being introduced by TsINAO. Software packages have been developed for optimal distribution of fertilizer resources among different parts of the country (FONUD), determination of rational fertilizer rates (RADOSE), preparing project estimates for liming (ISKRA), optimization of cattle and poultry diets (TROPA), and others.

As far as application of fertilizers and use of plant protection chemicals are concerned, farms are serviced primarily by district (interdistrict) production associations "Selkhozkhimiya", interfarm and local chemicalization stations set up directly at collective and state farms. Powerful and high-performance equipment has been supplied to the district production associations "Selkhozkhimiya", including handling machinery for transferring fertilizers from railroad warehouses to underground and other storage facilities, lime, fertilizer, and manure applicators, sprayers, dusters, and other machines.

Interfarm and local chemicalization stations have all the necessary equipment for timely application of fertilizers and plant protection chemicals. A chemicalization station must have a fertilizer storehouse, bulk blending plants, a facility for storing pesticides and other chemicals, machine sheds, and landing strips for agricultural aircraft. Such stations are manned by mechanized teams with several groups (truck fleet, manure application, fertilizer application, plant protection, chemical amelioration, etc.).

Chemicalization stations exercise continuous supervision of operations and ensure that the recommendations for rational use of all chemicals are met.

The high efficiency of chemicalization stations can be illustrated by many examples. For instance, according to an agrochemical service report (Derzhavin, 1980), specialization and intensification of chemicalization with properly managed stations ensure high yields at many farms. A case in point is the state breeding farm "Zarya kommunizma" in the Domodedovo district of the Moscow Region, where an average of more than 400 kg of inorganic nutrients, about 20 tons of organic nutrients, and 5 tons of lime are applied each year. The farm has a specialized chemicalization station. The average yields during the 1975-1978 period were as follows (in centners per hectare): winter wheat—50.6; spring cereals 49.9; potato 255.7; fodder beet—645.1; and perennial grasses (hay) - 82.1. During the 1966-1970 period, before the local chemicalization station was set up, the average yields were (in centners per hectare): grain cereals—34; potato—154; fodder beet and other roots—371; maize for silage—239; and perennial grasses (hay)—37.

At the collective farm "50-letie Oktyabrya" in the Markhamat district of the Andizhan Region, Uzbek SSR, improvements in cultivation as a result of creation of a chemicalization station have led to a cotton yield increase from 29.3 to 33.4 centners/ha, while at the Kalinin collective farm in the Thällman District of the Tashauz Region, Turkmen SSR, the increase was from 30.9 to 35.9 centners/ha.

In the State budget of the USSR for 1982, provisions were made for increasing the total turnover of organizations of the USSR State Committee for Agricultural Machinery and

the association "Soyuzselkhozkhimiya" of the USSR Ministry of Agriculture up to 24.4 billion rubles, or by 4.3 per cent, which, in turn, will enable considerably greater quantities of advanced machinery, inorganic fertilizers, and other material and technical means to be supplied to farms.

Chapter 2

Plant Nutrition

Nutrition in this context is essentially an exchange of substances between the plant and its environment. It implies translocation of substances from the surrounding medium (soil, air) into the plant tissue, where they are incorporated into complex organic compounds synthesized by the plant, and removal of some substances from the plant.

The supply of plants with carbon dioxide through leaves as a result of foliar nutrition is usually more steady than via root nutrition. Photosynthesis requires light, heat, humidity, and sufficient amounts of nutrients. The intensity, or rate, of the process is determined by the above factors plus the biological characteristics of plants and the thickness of their stand.

Root nutrition of plants depends not only on their biology and availability of photosynthesis products, but also on intensity of the root system growth, soil structure and aeration, moisture content, pH of the medium, content of nutrients in the soil, their forms and ratios, activity of the soil microflora, root exudates, and so on.

2.1 Chemical Composition of Plants

Plants build up their organism from certain chemical elements present in the environment. They consist of dry matter and a sizable amount of water. In most vegetative organs of farm crops, the water content amounts to 70-95 per cent, while in seeds it ranges from 5 to 15 per cent.

The water content in plant cells is a major factor governing the rate and direction of the vital processes in plant organisms. Inorganic nutrition conditions, water supply, and the biological characteristics of plants, in turn, determine the water content in the latter.

The dry matter of plants contains 90 to 95 per cent of organic compounds and 5 to 10 per cent of mineral salts.

The basic organic substances in plants include proteins and other nitrogenous compounds, fats, starch, sugars, cellulose, and pectins (Tables 2.1 through 2.3).

The quality of farm produce is determined by its content of the necessary organic and inorganic compounds. Various crops are grown for products with a certain content of

Table 2.1. Average Chemical Composition of a Cereal Kernel of Legume Seed (% dw)

Crop	Proteins	Starch	Fats	Cellulose	Sugars	Ash
Wheat	15	60	1.9	2.8	4.3	2.2
Rye	12	65	1.7	2.2	5.0	2.0
Oat	11	45	5.5	14.0	2.0	3.8
Barley	9	55	2.0	6.0	4.0	3.5
Maize	9	70	4.6	2.1	3.0	1.3
Rice	7	63	2.3	12.0	3.6	6.0
Millet	12	58	4.6	11.0	3.8	4.0
Pea	25	43	1.2	6.0	8.0	3.3
Bean	25	42	1.3	6.0	6.0	3.4
Soybean	35	3	20.0	5.0	10.0	5.8
Vetch	25	43	2.3	6.0	4.8	3.2
Kidney bean	20	55	1.8	3.8	5.2	3.3
Lentil	30	47	1.0	3.6	3.5	3.3
Lupine	32	3	5.0	16.0	2.0	3.8

Table 2.2. Average Chemical Composition of Seeds of Oil-Bearing Crops (% dw)

Chemical composition	Sunflower		Flax	Hemp
	whole seeds	kernels		
Fats	34	56	37	34
Proteins	16	26	26	22
Cellulose	25	6	8	19
Other carbohydrates	20	6	22	20
Ash	3.8	3.8	4	4

Table 2.3. Average Content of Basic Substances in Vegetables, Fruits, and Berries (% fw)

Crops	Sugars	Organic acids	Nitrogenous substances	Cellulose	Ash	Ascorbic acid (mg/100 g)
Cabbage	4.0	0.3	1.3	0.8	0.7	30
Cauliflower	3.0	0.1	2.5	1.2	0.8	100
Tomato	3.0	0.5	0.6	0.2	0.5	30
Sweet pepper	4.0	0.2	1.5	1.0	0.7	200
Eggplant	3.0	0.2	0.9	1.0	0.5	5
Cucumber	1.5	0.005	0.8	0.5	0.4	5
Onion	10.0	0.2	1.6	0.6	0.5	7
Garlic	0.5	0.2	7.0	1.0	1.0	15
Apple	9.0	0.7	0.4	1.0	0.4	25
Pear	10.0	0.2	0.4	0.8	0.4	15
Grape	18.0	0.7	0.7	0.2	0.6	6
Strawberry	18.0	1.4	1.4	1.2	0.5	50
Gooseberry	7.0	2.0	0.8	2.3	0.5	35
Currant	8.0	2.5	1.4	2.0	0.5	200
Cherry	9.0	1.8	0.9	0.2	0.5	17
Orange	7.0	1.4	0.9	2.5	0.7	65
Lemon	2.5	5.8	0.9	2.5	0.6	55

proteins, sugars, cellulose, vitamins, and other substances. For example, a high cellulose content in hay impairs its fodder properties, whereas such crops as cotton, flax, and hemp are grown to produce fibre which consists mainly of cellulose.

The quality of sugar beet is estimated from its sucrose content. Leguminous crops are classified by the amounts of protein they accumulate.

Plants and dry vegetable matter differ widely in elementary composition.

The bulk of living plants is constituted by oxygen (Table 2.4).

In the course of photosynthesis, carbon dioxide taken up primarily by leaves and water imported via roots forms in plants simple nitrogen-free organic substances consisting of carbon, oxygen, and hydrogen; proteins also contain nitrogen. Carbon, oxygen, hydrogen, and nitrogen constitute together 95 per cent of the dry matter of plants

Table 2.4. Average Content of Chemical Elements in Plants (wt. %) (according to Vinogradov)

Oxygen	70	Copper	2×10^{-1}
Carbon	18	Titanium	1×10^{-1}
Hydrogen	10	Vanadium	1×10^{-1}
Calcium	0.3	Boron	1×10^{-1}
Potassium	0.3	Barium	$n \times 10^{-1}$
Nitrogen	0.3	Strontium	$n \times 10^{-1}$
Silicon	0.15	Zirconium	$n \times 10^{-1}$
Magnesium	0.07	Nickel	5×10^{-5}
Phosphorus	0.07	Arsenic	3×10^{-5}
Sulphur	0.05	Cobalt	2×10^{-5}
Aluminium	0.02	Fluorine	1×10^{-5}
Sodium	0.02	Lithium	1×10^{-5}
Iron	0.02	Iodine	1×10^{-5}
Chlorine	0.01	Lead	$n \times 10^{-5}$
Manganese	1×10^{-3}	Cadmium	10^{-6}
Chromium	5×10^{-4}	Cesium	$n \times 10^{-6}$
Rubidium	5×10^{-4}	Selenium	10^{-6}
Zinc	3×10^{-4}	Mercury	$n \times 10^{-7}$
Molybdenum	3×10^{-4}	Radium	$n \times 10^{-14}$

(45% carbon, 42% oxygen, 6.5% hydrogen, and 1.5% nitrogen). These four species are termed energy elements.

When burnt, plants leave so-called ash elements constituting about 5 per cent of the dry matter.

The content of nitrogen and ash elements in plants depends on their biological characteristics and growth conditions and is dissimilar in different organs. For example, roots, stalks, and leaves contain more ash elements than seeds (Table 2.5).

The ash composition varies from plant to plant depending on their inorganic nutrition requirements. For example, in the ash of cereal grains the content of phosphorus (P_2O_5)* is as high as 50 per cent, in the ash of rice kernels, about 16 per cent, while in straw the phosphorus content is three to five times lower. The ash of straw and seeds of legumes is rich in sulphur, while that of potato tubers and root crops abounds in potassium (40-60% K_2O).

* The content of phosphorus and potassium in the ash of plants is usually expressed in terms of their oxides.

Table 2.5. Content of Basic Nutrients in Various Agricultural Crops (% of air-dry matter; % fw of root crops, vegetables, and green fodder) (according to Petukhov et al.)

Crop	N	Ash components				Total ash
		P_2O_5	K_2O	MgO	CaO	
Wheat:						
grain	2.50	0.85	0.50	0.15	0.07	1.7
straw	0.50	0.20	0.90	0.10	0.28	4.8
Winter rye:						
grain	2.00	0.85	0.60	0.12	0.10	1.8
straw	0.45	0.26	1.00	0.09	0.29	3.9
Maize (kernels)	1.80	0.57	0.37	0.20	0.03	1.5
Spring barley:						
grain	2.10	0.85	0.55	0.16	0.10	3.0
straw	0.50	0.20	1.00	0.09	0.33	4.5
Oat:						
grain	2.10	0.85	0.50	0.17	0.16	2.9
straw	0.65	0.35	1.60	0.12	0.38	6.4
Rice (kernels)	1.20	0.81	0.31	0.18	0.07	5.2
Pea:						
seeds	4.50	1.00	1.25	0.13	0.09	2.6
forage	0.65	1.15	—	0.14	0.35	1.4
Kidney bean (seeds)	3.68	1.38	1.72	0.29	0.24	3.9
Lupine:						
seeds	4.80	1.42	1.14	0.45	0.28	3.7
forage	0.55	0.11	0.30	0.06	0.16	0.9
Soybean (seeds)	5.80	1.04	1.26	0.25	0.17	2.8
Flax:						
seeds	4.00	1.35	1.00	0.47	0.27	3.3
straw	0.62	0.42	0.97	0.20	0.69	3.0
Sunflower:						
seeds	2.61	1.39	0.96	0.51	0.20	3.3
whole plant	1.56	0.76	5.25	0.68	1.53	10.0
Cotton:						
seeds	3.00	1.10	1.25	—	—	—
raw fibre	0.34	0.06	0.91	—	—	—
Sugar beet (roots)	0.24	0.08	0.25	0.05	0.06	0.6
Fodder beet (roots)	0.19	0.07	0.42	0.04	0.04	0.8
Potato (tubers)	0.32	0.14	0.60	0.06	0.03	1.0
Rutabaga (roots)	0.21	0.11	0.35	0.03	0.04	0.7
Fodder carrot (roots)	0.18	0.11	0.40	0.05	0.07	0.09
Cabbage (heads)	0.33	0.10	0.35	0.03	0.07	0.70
Tomato (fruits)	0.26	0.07	0.32	0.06	0.04	0.70
Grasses (meadow hay)	0.70	0.70	1.80	0.41	0.95	7.48
Alfalfa in early bloom	2.60	0.65	1.50	0.31	2.52	6.29
Red clover in bloom	1.97	0.56	1.50	0.76	2.35	5.38
Vetch in bloom	2.27	0.62	1.00	0.46	1.63	4.54
Timothy	1.55	0.70	2.04	0.20	0.49	5.91

Potassium accounts for 30 to 50 per cent of the elements in the ash of leaves of most plants, while in alfalfa, clover, and vetch the ash contains much more calcium than potassium. The content of potassium, phosphorus, and sulphur decreases in old leaves, whereas that of calcium increases from 20 40 to 50 60 per cent of the ash weight.

More than 70 elements have been found in plants. There is reason to believe that more exact and sophisticated analytical methods will reveal more. The elements essential for plant nutrition belong to different groups of the Mendeleev periodic system.

2.2 Essential Nutrient Elements

(Given in brackets are conventionally essential elements.)

I. H, (Li), Na, K, Cu, (Ag)
II. Mg, Ca, Zn, (Sr, Cd)
III. B, (Al)
IV. C, (Si, Ti, Pb)
V. N, P, V
VI. O, S, Mo, (Cr, Se)
VII. Cl, J, Mn, (F)
VIII. Fe, Co, (Ni)

At present, scientists distinguish between 20 essential nutrient elements and 12 conventionally essential ones. By definition, essential elements are those without which plants cannot complete their development cycle and which cannot be replaced by other elements. As regards the 12 conventionally essential elements, some experiments attest to their positive effect on plants.

The nutrient elements present in a plant organism in substantial quantities (from hundredths of a per cent to several per cent) are known as macronutrients. The elements present in amounts ranging from several thousandths to hundred thousandths of a per cent are termed trace elements or micronutrients, while the elements present in even smaller amounts are referred to as ultramicronutrients. Such a classification is rather arbitrary. For example, iron may be considered as a macronutrient from the standpoint of its content, while in terms of the functions it performs it belongs to micronutrients.

The micronutrient content in different organs follows a certain pattern. For instance, the content of manganese and molybdenum is usually high in leaves, while zinc, boron, cobalt, and copper, when present in sufficient amounts, are accumulated by both vegetative and generative organs. Grain crops are characterized by a relatively high content of boron in kernels in contrast to most legumes where it is accumulated in vegetative organs.

Various biological groups of plants differ widely in their requirements for optimal concentrations of individual micronutrients. For example, maize and tobacco need greater amounts of zinc, while grain crops require extra quantities of manganese.

The content and distribution of inorganic nutrients in plants determine the nutritive requirements of individual farm crops.

2.3 Plants as Accumulators of Individual Nutrient Elements

Many plants are capable of accumulating certain inorganic nutrients. This property must be taken into account in cultivation of various farm crops since it is a major factor of their nutritive value. The nutrients accumulated in plants are believed to be involved in some physiological and biochemical processes.

For example, molybdenum is accumulated by leguminous plants, and we are aware of the important role played by this element in the process of symbiotic fixation of atmospheric nitrogen. Boron is accumulated in beet which needs it for prevention of heart rot. The positive effect of sodium on beet yields is the reason why it is accumulated by this plant. Sulphur is accumulated by legumes and there is ample evidence of its involvement in protein metabolism. Thus, a relationship can be observed between the metabolism of nutrient-accumulating plants and their capacity to accumulate inorganic nutrients.

2.4 Nutrient Ratio in Plants and Yield Removal of Nutrients

The biological characteristics of plants and the conditions of their cultivation determine the removal of inorganic nutrients with crop yields.

Distinction is made between biological and yield removal of nutrients. In the latter case, nutrients are removed with the harvested crop, including grain and straw. The biological removal implies that nutrients are removed from the soil by all parts of a plant (harvested main product and by-products, crop residues, roots, and fallen leaves remaining in the field), see Table 2.6.

Table 2.6. Biological Removal of Nitrogen, Phosphorus, and Potassium by Different Crops (kg per ton of the main product)

Crop	N	P_2O_5	K_2O
Rye	40	15	44
Winter wheat	47	15	41
Spring wheat	51	15	39
Barley	36	14	38
Perennials (clover with timothy)	29	13	38
Late-grown potato	8	3	11
Pea	6	2	8
Cabbage	6	3	12
Cucumber	5	2	8
Tomato	5	2	5

The ratio of the nutrients required to build up a crop may vary widely depending on the crop and yield structure. For instance, when the percentage of straw increases in the biological yield of grain crops, it takes much more nutrients to obtain a ton of the main product (grain). In the case of potato, sunflower, cabbage, and sugar beet, a lot more potassium is required as opposed to grain crops. Clover and hemp are characterized by high calcium requirements (Table 2.7).

As a rule, kernels contain about four times as much nitrogen and phosphorus as straw does, while the content of

Table 2.7. Average Nutrient Ratios in Yields of Various Crops

Crop	N	P_2O_5	K_2O	CaO
Grain crops	2.5-3.0	1	1.5-2.2	0.5
Flax	2.0	1	1.5	1.0
Hemp	2.0	1	1.3	3-3.5
Clover	3.5	1	3.0	4.0
Potato	2.5-3.5	1	4-4.5	—
Sugar beet	2.5-3.5	1	3.5-5.0	—
Fodder beet	3.5-4.5	1	4.5-6.0	

potassium and calcium in straw is two to three times higher than in kernels.

The removal of nutrients with the harvested crop depends on the cultivation conditions. For example, to yield 100 centners of roots and the corresponding amount of tops in forest-steppe zones, sugar beet requires 50 kg N, 15 kg P_2O_5, and 60 kg K_2O. When grown in the Non-Black Earth zone, sugar beet produces more succulent leaves, and to yield 100 centners of roots it requires 80 to 100 kg N, 35 kg P_2O_5, and 145 kg K_2O.

Intensive application of inorganic fertilizers considerably increases the removal of all inorganic nutrients as the yields of farm crops continue to rise.

2.5 Import of Nutrients into Plants

Although plant nutrients nominally belong to environmental factors, they differ drastically from some others (temperature, pH, etc.) in that while being taken up by plants they undergo transition from an external, or environmental, to an internal factor of the plant organism.

There are recognized two types of nutrition of living organisms: autotrophic, that is, assimilation of mineral salts, water, and carbon dioxide, followed by synthesis of organic matter from these nutrients, and heterotrophic, that is, utilization by organisms of complex organic compounds. Animals and most microorganisms belong to heterotrophs. Plants, on the other hand, are autotrophic organisms.

It is through nutrition (aerial and via roots) that plants build their structural components, and if it is properly balanced, they rapidly gain in weight.

The life of a plant organism is governed by diverse metabolic reactions both with the surrounding medium and within a cell and among cells or different organs. The balanced import of individual chemical elements enables all biological reactions and physiological functions of the organism to proceed in a sequential and conjugated manner.

The basic process whereby organic substances are formed in plants is photosynthesis, although plants are also capable of taking up small amounts of amino acids, growth substances, vitamins, antibiotics, and carbon dioxide in the course of dark fixation. The inorganic nutrient uptake rate depends not only on the biological characteristics of a given plant and the environmental conditions (presence of sufficient amounts of available nutrients in the soil solution, appropriate temperature, soil aeration, etc.), but also on the amounts of photosynthesized energy and organic substances. The uptake of inorganic nutrients is limited by a number of factors. Plants take up 95 per cent and more of carbon dioxide via leaves and can receive from aqueous solutions ash elements, sulphur, and nitrogen by foliar nutrition. However, most of nitrogen, water, and ash elements enter plants from the soil via the root system.

Depending on the species and growth conditions, plants have root systems of different degrees of expansion. On poor soils and in drought-affected regions, plants develop aggressive roots in search for food and water.

Application of fertilizers usually reduces the weight ratio of roots to the above-ground portion of plants, although the size of the root system and its penetration depth become greater. Thus, fertilizing of farm crops not only enlarges the above-ground part of plants, but also produces a tangible positive effect on the development of roots.

The theory of inorganic nutrition took shape in 1858 when a plant was for the first time brought to full maturity in an artificial nutrient medium (water culture). Later, a complete nutrient mixture was proposed for growing plants in sand.

First speculations about the nature of nutrient uptake by the living cell were made by Dutrochet (1837) who held that the penetration of water and the solutes it contains into cells proceeds by way of diffusion across porous cytoplasmic membranes.

Sachs set forth the concept of "cumulative diffusion" after his observations that the chemical processes occurring in cells constantly upset the equilibrium between the concentrations of substances inside the cells and in the external solution.

The diffusion-osmotic theory was propounded by Pfeffer, de Vries, Meyer, and other scientists. According to this theory, nutrients are aspirated into plants through roots together with water which constantly transpires. Thus, the import of nutrients is directly dependent on the transpiration rate of plants. However, the data available at that time concerning the translocation of nutrients into plants were at variance with the diffusion-osmotic theory.

The lack of a definite relationship between imbibition of water by plants and their uptake of nutrients was pointed out already by Timiryazev who wrote that for their nourishment plants do not require the huge amounts of water they eventually lose by transpiration. This idea was supported and elaborated by Sabinin. He demonstrated that the small amounts of nutrients present in the nutrient solution are accumulated perceptibly in the bleeding sap of plants.

Late in the 19th century, Overton came up with the lipid theory stating that nutrients find their way into the cell by dissolving in the lipid components of cytoplasmic membranes. He established a correlation between the rate of penetration of basic aniline dyes into plant cells and their solubility in lipids.

Traube and Ruland, authors of what became known as the ultrafiltration theory, contended that the penetration of nutrients across the cytoplasmic envelope depends on the sizes of its pores and molecules. Dravert observed that the penetration of the acid dyes under examination depended on the size of their molecules. However, such facts as the uptake of the large molecules of amino acids, phytin, and other organic substances by plants cannot be reconciled with this theory.

Early in the 20th century, Devault found that cations can be readily bound by plant cells from highly dilute solutions. This finding has given impetus to the emergence and elaboration of the adsorption theory. It was shown that by virtue of mutual equivalent exchange bound cations may be forced back from the tissues by other cations. Thus, while some ions are taken in, others are displaced, this process being dependent on concentration and time.

In most of their investigations, Sabinin and other scientists traced a relationship between uptake of substances and the level of vital activities of cells and showed the active role of the root system in nutrient absorption. The content of substances in the bleeding sap of plants depends on their supply with nutrients and on the plant species and age. The different physiological activity of cells and tissues is responsible for their dissimilar chemical composition and electric properties.

The metabolic rate of tissues determines the nutrient uptake rate. Steward, Lundegaard, Burstrem, and other research workers have established a close relationship between the respiration of tissues and the uptake of ions of mineral salts. It was demonstrated that the uptake of nutrients by plant cells and tissues is enhanced by improved aeration of the nutrient solution, introduction of glucose, creation of temperature and other conditions conducive to activation of the respiratory process.

Sabinin corroborated the correlation between plant nutrition and formation and development of individual organs.

In this brief review of inorganic plant nutrition research, the following theories have been outlined: diffusion-osmotic, lipid, ultrafiltration, and adsorption theories.

The above theories have to some or other extent contributed to the evolution of the ideas concerning the import of nutrients into plants. Being basically correct, they provide an overall though somewhat simplistic picture of inorganic nutrient uptake.

In recent decades, the theory of inorganic nutrient uptake by plants has been considerably advanced and in its present form includes some of the basic concepts set forth in the earlier theories.

2.6 Forms of Nutrient Compounds Taken Up by Plants

As a result of continuous biological, physical, chemical, and physicochemical processes in the soil, complex inorganic or organic substances break down into simple substances. The resulting products are constantly involved in plant nutrition, although part of them may be lost in the gaseous form or leached into the underlying horizons or whatever

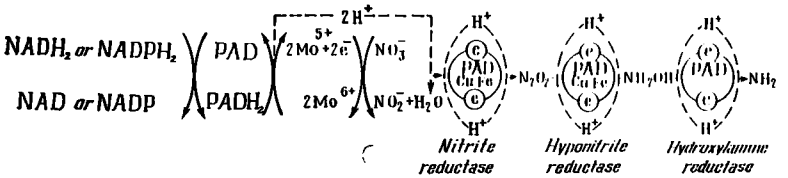


Fig. 2.1: Nitrate reduction

rivers and lakes may be nearby, as well as undergo fixation by the soil without any exchange. Most nutrients are taken up by plants in their ionic (anionic or cationic) form through roots. In addition, plants may use insignificant amounts of amino acids, sugars, sucrose phosphates, and other organic compounds for their nutrition. Once in plants, amino acids undergo deamination, and the liberated ammonia is utilized in syntheses. However, nitrogen is taken up primarily in the form of the nitrate anion NO_3^- and ammonium cation NH_4^+. These ions are constantly produced in the soil by organic substances as a consequence of the ammonification and nitrification processes initiated by microorganisms.

The nitrogen taken up in a nitrate form is reduced to ammonia by a group of enzymes.

The reduction of nitrates to nitrites requires two protons and two electrons. After attachment of the electrons, nitrates transform to nitrites. The subsequently forming compounds include hyponitrite, hydroxylamine, and ammonia. It takes a total of eight protons and as many electrons to reduce nitrates to ammonia (Fig. 2.1).

Nitrogen in the form of ammonia is utilized by plants in the reaction of substitution of the oxygen in the carbonyl

group of the keto acid, yielding a corresponding amino acid:

$$\underset{\text{keto acid}}{R-\overset{\overset{O}{\|}}{C}-COOH} \longrightarrow \underset{\text{amino acid}}{R-\overset{\overset{NH_2}{|}}{CH}-COOH}$$

In the overall budget of bound nitrogen forms actively involved in the natural cycle of this element, the process of molecular nitrogen fixation is of paramount importance. The atmospheric nitrogen is fixed by a number of soil microorganisms and many plants in symbiosis with microorganisms (Fig. 2.2).

Nitrogen fixation occurs in steps. Important functions at different steps of the process are performed by the enzyme nitrogenase, leg-hemoglobin, compounds belonging to the vitamin B_{12} group, and metals (iron, molybdenum, cobalt, copper, etc.).

Nitrogen and sulphur are constituents of proteins and many other compounds. Sulphur is taken up by plants in the form of the sulphate anion SO_4^{2-}. In plants, the sulphate is reduced first to sulphite (SO_3^{2-}) and then to sulphide (S^{2-}), the latter attaching a hydrogen to form sulphydryl groups (S—H). Two sulphydryl groups lose their hydrogens to produce a disulphide group (—S—S—). Sulphur forms part of acetyl coenzyme A (involved in lipid synthesis), amino acids (cysteine, cystine, and methionine), and other compounds of great biological importance.

Phosphorus is taken up in the form of the phosphate anion ($H_2PO_4^-$), (HPO_4^{2-}), or (PO_4^{3-}). In plants, phosphorus is included in nucleic acids, which constitute the genetic apparatus of the nucleus, phospholipids, determining the properties of cell membranes, and some coenzymes (pyridine nucleotides and nucleoside phosphates among others). Phosphorus enters living organisms in the form of the orthophosphoric acid residue, where it remains as is or combines with organic molecules (primary phosphorylation), or else the acid residue passes from one molecule into another (transphosphorylation). Adenosine phosphates play an important role in all vital processes as sources of energy.

The primary metabolization of the phosphate is associated with its extremely rapid (a few milliseconds) entrainment

into nucleotide synthesis. After longer periods of time (10 min), phosphorus is found in nucleic acids. In more than three hours, when the metabolic pool of phosphorus acceptors is saturated, phosphorus may enter the vacuole in

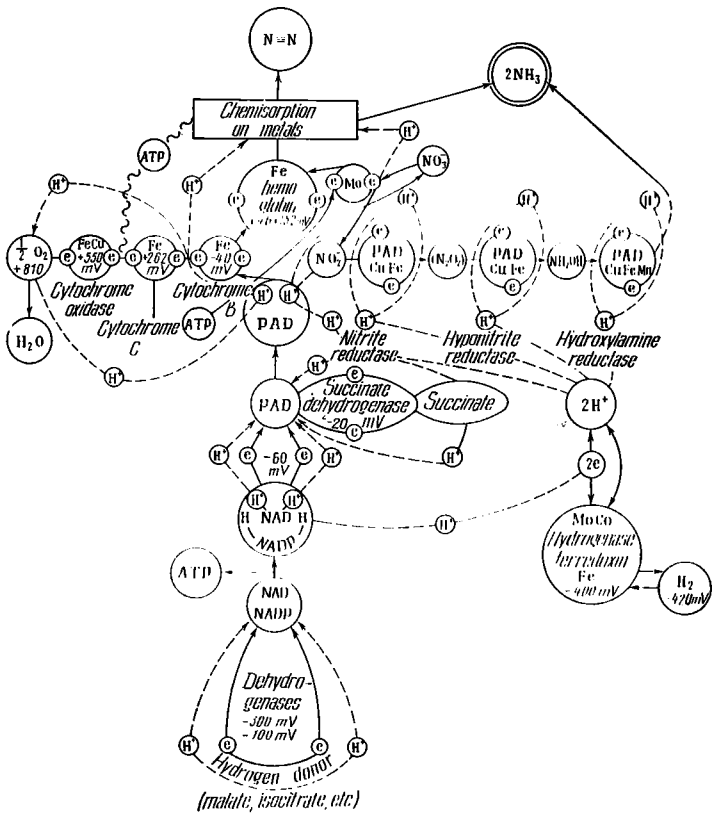


Fig. 2.2: Molecular nitrogen fixation in the nodules of leguminous crops (Peive, Yagodin, Zhiznevskaya)

inorganic form. Under anaerobic conditions, accumulation of phosphorus acceptors not utilized in respiratory metabolism takes place, hence accumulation of greater amounts of phosphorus in roots with oxygen deficiency.

Chlorine is imported into plants as the ion Cl. Many plants may contain chlorine in high concentrations without being adversely affected by it. This is primarily true as regards salt-tolerant plants known as halophytes.

Boron and molybdenum are taken up by plants in the form of anions (borates and molybdates).

Calcium, potassium, magnesium, copper, iron, and zinc enter plants in the form of respective cations, while manganese does so in the form of manganate cations and anions.

In many vital processes, transitions of the cytoplasm from gel to sol play an important role. Ions of alkali metals (K^+, Na^+) increase, and those of alkaline-earth metals (Ca^{2+}, Mg^{2+}) decrease, the hydration of the cytoplasm.

Cytoplasm is constituted by negatively charged hydrated proteinaceous colloid particles. They attract the positively charged poles of water dipoles to the colloid particles. The cations that are transported into the cytoplasm are also surrounded by a hydrate envelope. Being more heavily charged, divalent cations come closer to the negatively charged proteinaceous colloid particles and neutralize them. As a consequence, the hydrate envelope disappears, and the protoplasm becomes more viscous.

Because of the weak attraction, univalent cations stop short of the proteinaceous colloid particle and no charge neutralization takes place with the result that the cytoplasm is better hydrated at a higher potassium ion content.

High concentration (50 to 100 mM) of potassium ions is typical of all plant and animal cells. Only a certain potassium ion content in the cell can sustain the normal course of such processes as biosynthesis of protein, photosynthesis, respiration, and synthesis of polymer compounds (starch, fats, and carbohydrates).

Note that ions enter the root and are translocated in cells not only to "deliver" certain building materials to particular sites where some or other molecules are biosynthesized. Any movement of ions is important per se for it redistributes electric charges in the cell and changes the electric and concentration gradients. All these changes govern the processes that occur in cells.

2.7 Root and Its Specialization as an Absorption Organ

The root is the specialized portion of a plant anchoring it in the soil and performing the functions of absorption, metabolization, distribution, and transport of water and inorganic nutrients. It is an organ in which numerous biosynthetic processes occur and which performs some special functions.

The extent and pattern of root development determine to a great degree the capacity of plants to take up nutrients. A common feature is that the bulk of nutrients is absorbed by young, growing portions of the root.

The growth zones of a root consist of the division zone (meristem) in which cells are not yet differentiated into tissues, the expansion zone, and the root hair zone with pronounced xylem and phloem elements as well as the epidermis with root hairs (see Fig. 2.3).

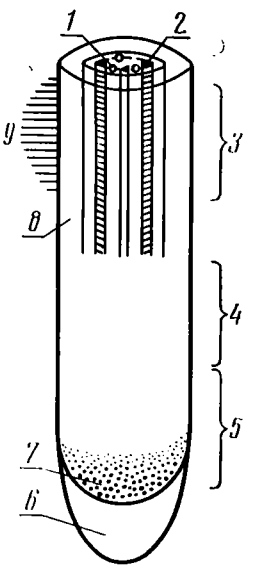


Fig. 2.3: Root structure
1—phloem; *2*—xylem; *3*—root hair zone; *4*—expansion zone; *5*—division zone; *6*—root cap; *7*—apical meristem; *8*—dermatogen; *9*—epiblem with root hairs

The functions of the root are not confined to absorption and translocation of water and inorganic nutrients. The root system is also responsible for the synthesis of some physiologically active substances, amino acids and proteins. Nutrients are not transported in their entirety into the above-ground organs of plants; part of them are involved in the synthetic processes occurring in the root system itself. Inorganic nutrients are most intensively absorbed by the cells of the root hair zone, as opposed to the division and expansion zones.

The root system of field crops has an immense absorbing surface. The root surface, including its active portion, be-

Table 2.8. Variations in the Root Surface of Spring Wheat

Development stage	Root surface (in m²) of a single plant		Ratio between the active and inactive surface portions
	total	active	
Tillering	9.60	4.91	1.05
Shooting	29.39	10.81	0.59
Early flowering	36.73	17.07	0.86
Late flowering	40.09	24.76	1.30
Gold ripeness	30.86	14.80	0.92

comes most developed during the flowering period as a rule (Table 2.8).

The absorbing surface of the root is substantially extended by root hairs. The root hair zone is believed to be the zone of absorption. However, as was shown experimentally, nutrients may be absorbed along the root at distances of 0.5 m and even 1 m from the root tip, that is, along the portion devoid of root hairs.

In the experiments conducted by Russell and Clarkson, phosphates translocated from points 40 and more centimetres distant from the root tip of barley covered the same distance as those translocated in the root hair zone.

As can be inferred from Clarkson's experiment, root hairs do not exhibit any special absorbing capacity. If barley is grown in an aqueous solution subjected to intensive aeration (by continuous stirring), no hairs form on roots, yet the absorption of ions continues unabated. The main function of root hairs seems to be maximal extension of the root surface for plants to be supplied with phosphorus in the first place. As is known, the migration of phosphorus in the soil is extremely slow, while the rate of its absorption by plants is high. Within a short period of time, roots absorb all of the surrounding phosphorus and extend their surface to absorb additional amounts of this element. Other ions are more mobile than phosphorus, and root hairs are less needed for their absorption. It should be pointed out that, in accordance with the laws of chemotropism, the root grows and extends in the soil towards the higher nutrient concentration.

As plants extend their root system in the course of vegetation, their penetration into the soil expands, and roots come in contact with additional amounts of soil nutrients. As a result of active absorption of water by roots, the soil solution constantly moves rootwards.

Should the solution concentration decrease because of intensive nutrient uptake by plants, nutrients move towards the root, governed by the laws of diffusion.

The activity of the root system is closely associated with the above-ground organs. (We consider root and aerial (foliar) nutrition separately merely for convenience.)

Assimilates in the form of sucrose are transported from the lower fully grown leaves into roots. By utilizing sucrose, the root can successfully synthesize the entire range of the compounds constituting the cells that perform its basic functions.

The sucrose transported into the root is involved in the following processes: (1) metabolism of the root itself, its growth, and maintaining the functioning cells in a physiologically active state; (2) synthesis of the compounds exuded by the root into the surrounding soil; and (3) synthesis of the substances carried with the sap into the above-ground organs, that is, providing for the synthesizing activity of the root.

The organic acids present in roots are highly diverse and owe their origin to the transformations of the sucrose translocated into the root. Plants lose small amounts of assimilates with root exudates. For example, roots of legumes exude only 0.5 to 0.7 per cent of the carbon (as organic compounds) taken up by leaves in the form of carbon dioxide. Root exudates have been found to contain sugars, amino acids, organic acids, and, in smaller amounts, vitamins, enzymes, and volatile organic compounds such as ethylene. The secreting function of the root is associated with the absorption of nutrients. For instance, by virtue of the acidulating effect of root exudates, lupine more readily absorbs phosphorus from difficultly soluble compounds.

Root exudates differ in the amounts and content of their components, which is determined by the plant species and varieties. For example, root exudates from legumes are richer in amino acids than those from cereals.

Accumulation of root exudates in isolated roots cultivated under sterile conditions inhibits their growth. This inhibition is due to accumulation of amino acids, i.e. the basic component of root exudates, to concentrations toxic for plants.

In 1940, Sabinin brought forth the concept of transformation of substances as they pass through the root, followed by that of the synthesizing activity of the root. The essence of this concept is as follows:

1. The root is capable of not only absorbing inorganic nutrients, but also converting them fully or partially with subsequent export of the converted forms into the above-ground organs.
2. The synthesizing activity of the root is sustained by the assimilates imported into it or, in other words, is determined by photosynthesis.
3. The root influences the above-ground organs by supplying them not only with water and inorganic nutrients, but also with products of the specific reactions of root metabolism, such as non-auxin phytohormones.

The growth substances present in the bleeding sap contain, primarily, cytokinins, which are believed to be a factor responsible for intensive metabolism in leaves and slowing down their senescence. Cytokinins are synthesized mainly in the root and, partially, in leaves.

Gibberellins are indispensable for stalk growth. The discontinued growth of the above-ground organs, following removal of the root, is due not only to the reduced supply of nutrients, but also to the cessation of cytokinin and gibberellin import from roots. The formation of aerial roots on plant stems and trunks during active growth may be explained by the need in sources of cytokinins and gibberellins.

Interestingly, as plants senesce, the calcium content in their cells increases, while that of potassium decreases. The presence of large amounts of K^+ ions is typical of young, actively functioning plant organisms. An important finding is that treatment of plants with the growth substance kinetin is conducive to export of Ca^{2+} ions from cells and accumulation of K^+ ions. Yellowing leaves turn green again, the subcellular structures stop degenerating, and the biosynthesis of protein is intensified considerably.

2.8 Theory of Nutrient Uptake

Nutrients are exchanged between the plant and environment via the surface cells of the root system and aboveground organs. As is known, plant cell walls are easily permeable (the radius of mineral salt ions ranges from 0.4 to 0.6 nm, whereas the average radius of cell wall channels is 5 to 20 nm), and if they had been the only barrier between the root and the external nutrient solution, the ion concentration would have been equalized merely through diffusion. However, nutrients are present in plant organisms in much higher concentrations than in the surrounding nutrient solution. Moreover, the import of individual nutrients and their accumulation proceed differently and do not conform to the nutrient ratio in the nutrient solution. This is due to the plasmalemma which prevents loss of the substances accumulated by the cell through diffusion, while at the same time allows water and inorganic nutrients to be translocated inside (Fig. 2.4).

The translocation of substances against the concentration gradient requires energy.

As has been mentioned above, several theories account for the import of nutrients into cells. However, the complex process of translocation of nutrients into the root system cannot be explained by a single hypothesis or theory. Several uptake mechanisms seem to be involved in plants, the continuously changing combination of which is responsible for the course of the process, one mechanism complementing another.

By consensus, the transport of nutrients into the cell is currently believed to involve two mechanisms, i.e. passive flow of substances following the electrochemical gradient and their active transfer against the gradient. Since ions carry an electric charge, their distribution between the cell and external solution is determined both by the electric potential difference and by the difference in concentrations. These two factors are usually referred to as *electrochemical gradient.*

The contribution of different mechanisms of assimilate transport may vary throughout the plant ontogeny and is governed by many factors. For example, the role of the pas-

sive flow of ions gains in importance when the external salt concentration increases (which may occur in salinization or local application of fertilizers).

It should be noted that the term "active transport" of ions was previously used to imply the movement of cations and anions responsible for metabolism. It is therefore assumed

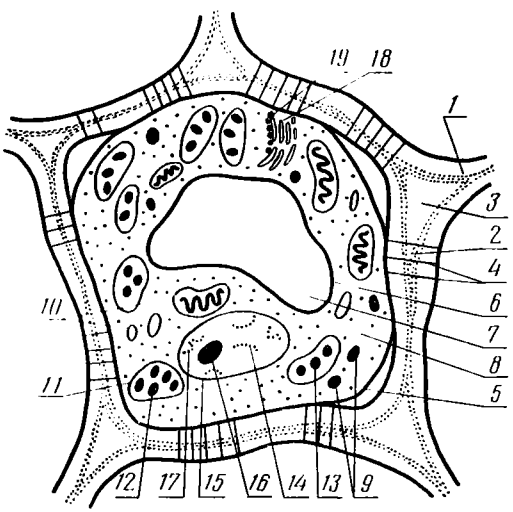


Fig. 2.4: Plant cell structure

1—cell wall; *2*—median plate; *3*—intercellular space; *4*—plasmodesmata *5*—plasmalemma; *6*—tonoplast; *7*—vacuole; *8*—cytoplasm; *9*—lipids; *10*—mitochondria; *11*—chloroplast; *12*—chloroplast grana; *13*—starch grain in chloroplast; *14*—nucleus; *15*—nuclear envelope; *16*—nucleolus; *17*—nuclear chromatin network; *18*—Golgi apparatus (dictyosomes); *19*—ribosomes

that the movement of ions following the gradient of electrochemical potentials determined by the ion charge and difference in concentrations is passive, whereas their movement against the gradient is active.

Free Space. Ions move across the cell envelope towards the plasmalemma by way of diffusion or together with the solvent in a flux of solution. The transpiration of water by leaves ensures direct passage of the water and solutes it contains in a flux across the cell envelope; however, this process has to do with ion transport only when the transpiration is very intensive, for example, on a hot summer day.

Diffusion, or movement of gas, liquid or solute molecules following the concentration gradient, depends on the solute concentration gradient and the area traversed by the compounds or ions. The incessant diffusive passage of ions across the plasmalemma gives rise to a continuous influx of new ions towards the latter in order to equalize the concentration.

The part of the total volume of the root system tissues, through which ions move in and out as a result of diffusion, is called *free space*. It constitutes about four to six per cent of the total root volume and is confined within the loose primary envelope of the cell walls beyond the protoplast, outside the plasmalemma.

The free space is, in turn, divided into the "water space" from which ions may be diffusively translocated into water and the "Donnan space" from which ions are exported by way of exchange only into the salt solution. The envelope of root cells consists of a loose surface layer with a system of pores or channels about 20 nm in diameter. The root cells are charged negatively with respect to the external solution. The negatively charged walls of the free space pores or channels attract and retain cations but repulse anions. Already at this level, the selective absorption of ions becomes manifest to some or other extent. In the central portion of such a channel, the concentration of cations is equal to that of the external solution. This portion may be ascribed to the water space.

The exchange, or Donnan, space is located closer to cell walls, where cations are accumulated because of the negative charge of the walls.

The translocation of nutrients into the free space is fast and follows the saturation curve as their concentration increases (Fig. 2.5). Its selectivity is low, and the final rate remains constant in the presence of inhibitors and at lower temperatures. This is a reversible process in which no diffusion barriers are involved. The negatively charged membrane may be either the cell wall with carboxyl anions of protopectin or the plasmalemma, probably serving as the delimiting membrane of the free space with negatively charged portions of protein and phospholipid molecules. At this stage of the translocation exchange adsorption plays an important role. For example, a root kept in a solution con-

taining Ca^{2+} and then transferred into another one containing K^+ loses the adsorbed calcium as a result of exchange adsorption. The vast network of intercellular spaces in the plant tissue provides additional pathways for transport. The loose cellulose envelopes of plant cells not only perform protective and mechanical functions, but also create myriad microscopic sites for adsorption and passive flow of substances along the tissue from which cells obtain the necessary nutrients. As has already been mentioned, the substances brought by diffusion into the free space may undergo primary exchange adsorption there, i.e. they may be displaced from the free space into the external solution or into the cell. The physicochemical principle of the adsorption process resides in that cell envelopes immobilize nutrients and retain them as ions by forces of electrostatic attraction.

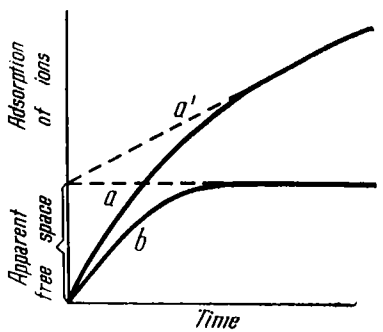


Fig. 2.5: Labelled ion absorption pattern after transferring roots from pure water into a salt solution

a—normal pattern (non-metabolic + metabolic absorption); *b*—at 0 °C or in the presence of respiration inhibitors (only non-metabolic absorption); *a'*—metabolic absorption

Consequently, the free space is the portion of the nutrient medium and, at the same time, an adsorption zone in which cells derive all the nutrients necessary for their normal metabolism. Next, depending on the metabolic rate and pattern, the adsorption becomes selective. The influx of nutrients into the free space should be regarded as a step preceding adsorption rather than adsorption itself.

The cellulose envelopes of all plant cells are interlinked forming a vesicular system known as apoplast. As a result of foliar transpiration, roots imbibe water and mineral salts in a mass flow, sending them into the intercellular spaces. In order to reach the xylem vessels for subsequent transport into the above-ground organs, nutrients must cover a long distance in a radial direction across the root. This

apoplastic pathway of ions, however, is interrupted by Casparian strips, i.e. waterproof bands in which cell walls are impregnated with suberin, a substance impermeable to aqueous solutions. However, some ions reach the conducting vessels following an extracellular path, via "passage cells" whose envelope is free of Casparian strips. Furthermore, in the growing root tip, the endoderm with Casparian strips has not yet formed and therefore, ions can penetrate extracellularly, by-passing cell membranes. It should be noted, however, that only a few ions enter the plant apoplastically, and the role of the apoplast in the nutrient balance under normal conditions is apparently insignificant.

If an ion has traversed the cell membrane (plasmalemma), its further path involves another cell system known as symplast where it travels from cell to cell by virtue of the fact that the protoplasts of all cells are bridged by plasmodesmata ensuring contact between the plasmalemmas of different cells. The plasmodesmatal mechanism permits regulating the transport rate of the nutrients travelling via the symplast. The usual transport rate of ions, amino acids, and sugars is 2 to 4 cm/h.

Cytoplasmic Membrane (Plasmalemma). The membrane determines the capacity of a cell for selective uptake of ions. It can initiate nutrient and energy metabolism reactions. The contact of the cell with the surrounding medium is through the cytoplasmic membrane, or plasmalemma. At the same time, the plasmalemma is involved in many other functions of the cell. According to modern concepts, the cell membrane consists of two phospholipid layers joined at their hydrophobic ends. At certain portions, proteins are embedded into the phospholipid molecules, that is, the plasmalemma is essentially a bimolecular phospholipid layer with embedded carrier protein molecules (see Fig. 2.6). Phospholipids, which are the basic component of membranes, may form several types of liquid-crystal structures (Fig. 2.7).

Phospholipid molecules have polar "heads" (hydrophilic groups) and nonpolar "tails" (long hydrophobic hydrocarbon residues). Phospholipids are poorly soluble both in a polar solvent, such as water (because of the nonpolar "tails") and in a nonpolar medium, such as oil (because of the polar

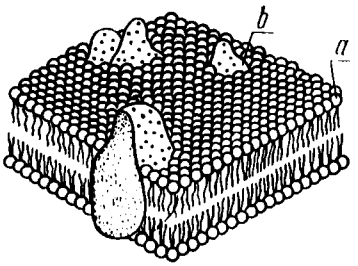


Fig. 2.6: Mosaic model of cell membrane

a lipids; *b*—proteins. By virtue of the mosaic structure of the cytoplasmic membrane, some of its portions are charged positively and negatively, which allows cations and anions to be absorbed from the surrounding medium (Bergelson, 1975)

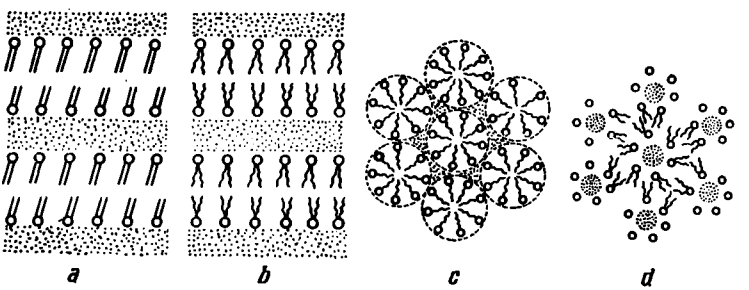


Fig. 2.7: Lipid aggregate structure

a—gel-like; *b*—lamellar (layered); *c*—lipid cylinders in water; *d*—water cylinders in lipid phase. The basic membrane components are phospholipids which may form several types of liquid-crystal structures (Bergelson, 1975)

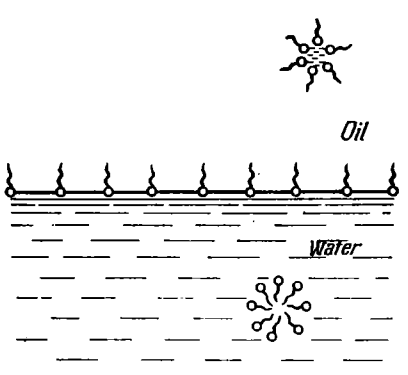
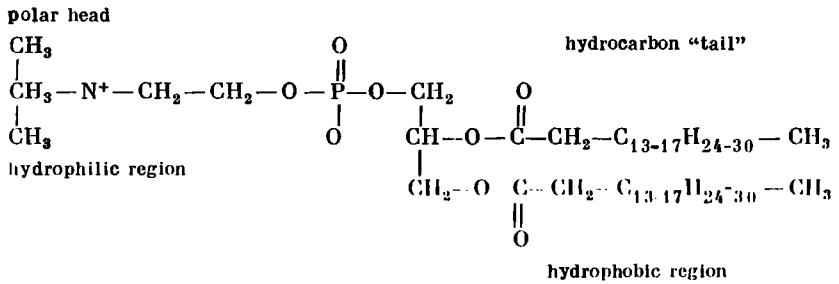


Fig. 2.8: Monomolecular lipid layer at the water-oil interface and lipid micelles in oil and in water. Formation of the monomolecular layer at the interface restricts the permeability of substances (Bergelson, 1975)

"heads"). The monomolecular layer at the phase boundary restricts the ability of substances to permeate (Fig. 2.8).

The structural organization of phospholipids is exemplified by the chemical structure of phosphatidyl choline:



The bilayer membrane is 10 to 12 nm thick. The presence of a certain amount of negatively charged heads in the lipid micella of the membrane creates a potential difference across the lipid-water boundary. Therefore, positive ions are attracted by the membrane surface, while negative ions are repulsed.

At present, most workers regard the membrane as a phospholipid structure studded with proteins. It appears either as a plain film or as spherical micellae.

Proteins are essential membrane components. They also serve as the structural material of the pores lining the channel walls in the membrane. The cytoplasmic membrane is not only a barrier, but also a site where the absorbed ions are involved in various metabolic reactions. Part of the membrane proteins are catalytically active and exhibit enzymic properties. The membrane proteins in the form of globules have a hydrophobic anchor, that is, part of the molecules are capable of interacting with lipids. Proteins may be linked with the polar heads of membrane lipids via the bridges formed by cations of bivalent metals (Fig. 2.9).

A protein globule floats in the liquid bilayer of the membrane and may move both horizontally and vertically.

Membrane Permeability. Solute molecules move incessantly in a chaotic manner throughout the solution, colliding with other molecules, including those of the solvent.

If a membrane separates two solutions of different concentrations, then, depending on its permeability, either the solvent or solutes will pass through it and the concentrations will be equalized through diffusion (Figs. 2.10 and 2.11).

The membrane of any cell in the absorbing zone of the root is traversed by hundreds of various substances at a

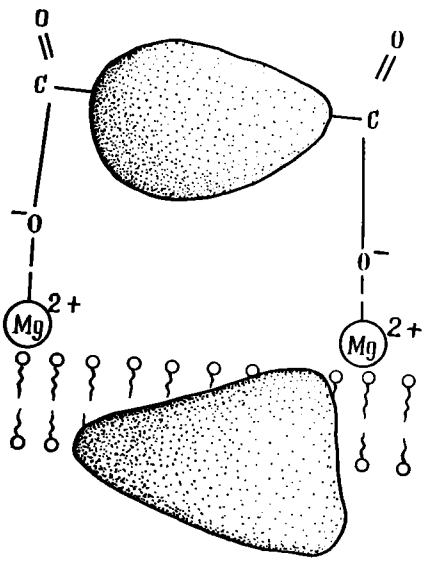


Fig. 2.9: Linkage of negatively charged proteins and polar heads of membrane lipids across bridges formed by bivalent metal ions. The proteins may be linked with the polar heads of membrane lipids indirectly, via bridges formed by cations of bivalent metals (Bergelson, 1975)

time, including those soluble not only in fats but also in water.

Passive transport of these substances may proceed if membranes are assumed to have hydrophilic orifices (pores). Nonspecific passive transport of ions and molecules may occur via diffusion through the membrane pores (in the case of hydrophilic substances), while that of neutral molecules, also by way of dissolution of the penetrating substances in the membrane (in the case of substances readily soluble in fats).

Calculations show that the area of pores in the membrane must not exceed 0.1 per cent of its surface.

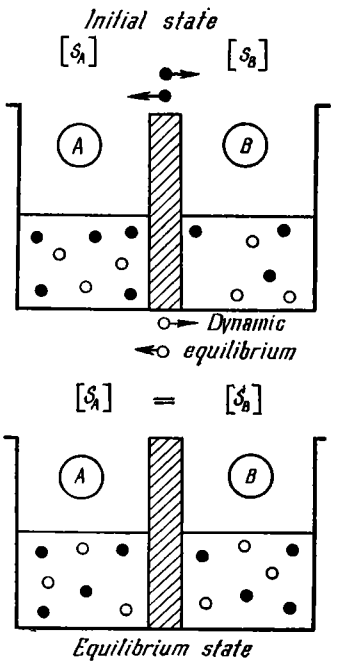


Fig. 2.10: Solute molecule distribution as a result of diffusion across a permeable membrane. S_A and S_B are solute concentrations in chambers A and B, respectively. Full circles indicate solute molecules; open circles stand for water molecules. At first, pure transfer of the substance across the membrane is observed (upper drawing), then dynamic equilibrium is established without any pure transfer (bottom drawing). (Clarkson, 1978.)

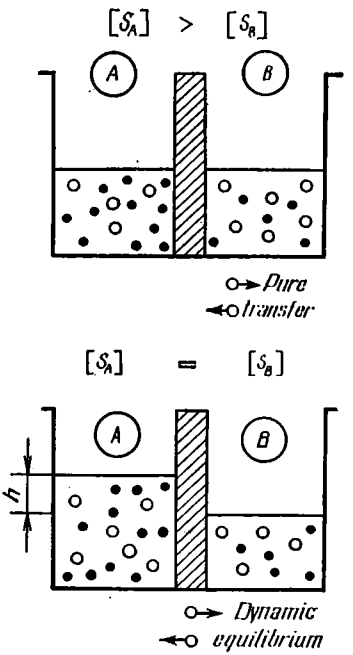


Fig. 2.11: Transfer of water molecules across a semipermeable membrane dividing two chambers filled initially with a dissolved substance (full circles) in different concentrations. At first (upper drawing), pure transfer of the water molecules (open circles) into chamber A is observed, since the membrane is impermeable to the solutes. Upon achievement of a steady state (bottom drawing), the levels of the solutions in chambers A and B are different, the amount of the difference being proportional to the initial solute concentration difference (osmotic potential) (Clarkson, 1978)

Transport of particles carrying electric charges depends on the concentration and electric potential gradients.

For example, when common salt solutions of different concentrations are used, Cl^- and Na^+ ions rush from the more concentrated solution into the more dilute one. However, since Cl^- ions are more mobile in an aqueous medium,

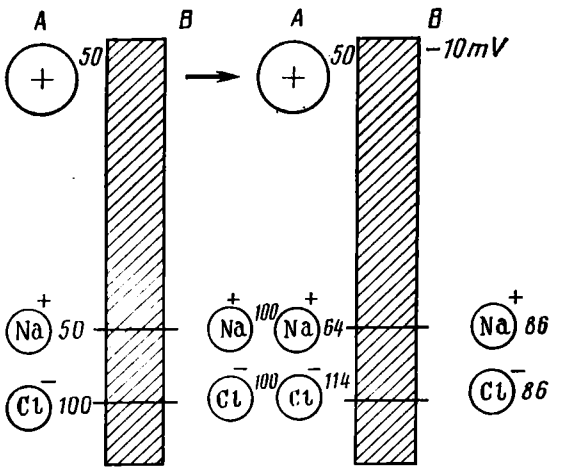


Fig. 2.12: Pattern of ion transfer across semipermeable membranes. When cations in one of the solutions (A) are too large to pass across the membrane, chloride ions from the second solution (B) start to enter the first one, following sodium ions, in spite of the fact that their migration is against the concentration gradient. A potential difference occurs across the membrane. The large circles stand for the cation that cannot pass (protein). Numerals indicate the relative ion concentrations at which the potential difference is about 10 mV

the more dilute solution will soon become negatively charged with respect to the solution with the higher concentration. A potential difference (diffusion potential) arises between the solutions. If a membrane permeable to some ions and impermeable to others is placed between them, a membrane potential will emerge (Fig. 2.12).

Knowledge of the direction of the electrochemical potential gradient is necessary to elucidate the ion transport mechanism. For cations, this gradient is oriented inwards,

into the cell or root, whereas in the case of anions its orientation is outwards. Determinations of the intracellular concentrations of cations usually give a value higher than would be inferred theoretically on the basis of diffusion. According to the law of passive transport, anions cannot enter cells, yet they are accumulated in root cells and in the bleeding sap.

Carrier Hypothesis and Ion Pumps. In recent years, it has been speculated that nutrients enter the root primarily in the form of ions, after which they are invariably translocated across the cell plasmalemma. This translocation may be passive, that is, following the electrochemical gradient, or active, that is, against the gradient.

Of greatest importance is the mechanism of active transport of ions across phospholipid membranes.

The selectivity of ion uptake, the increasing ion concentration in cells, and the competition among chemically related ions as they are being absorbed by root cells can be explained in light of the carrier theory. According to this theory, ions traverse membranes as complexes with a carrier molecule rather than in a free state. These complexes dissociate on the inner side of the membrane, and the ions are released into the cell. Ions can be imported into cells with the aid of carriers of various types.

The motive force of carrier-assisted transport may be, just as in the case of passive transport, either the chemical gradient of the substance or its electrochemical potential. Here substances move "downhill", and the process is known as facilitated diffusion. Facilitated diffusion in a system must eventually lead to equalization of the gradients and establishment of an equilibrium in it. The absence of facilitated diffusion systems for intermediate products of metabolic processes in biological membranes stems from the fact that these intermediate products must remain inside cells and respective organelles.

Facilitated diffusion drives substances down the concentration gradient but at a fast speed. Usually, ions pass across phospholipid membranes at the same speed as through a water layer.

In fungi, algae, and bacteria, the function of carriers may be performed by some antibiotics, such as valinomycin

whose molecule contains six carbonyl groups >C =O with negatively charged oxygens. The complex of valinomycin with potassium is highly hydrophobic, because the hydrocarbon residues are oriented outwards, and readily soluble in the hydrocarbon portion of the membrane. This is why valinomycin considerably increases the permeability of membranes to potassium, forming in them what may be called a "potassium hole".

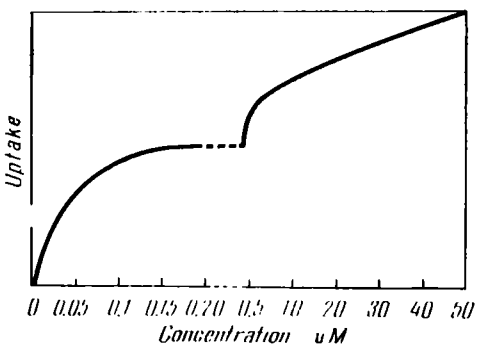


Fig. 2.13: K^+ absorption by barley roots versus solution concentration. The trend of the curve is indicative of two different transfer mechanisms (according to Epstein)

The ionic permeability of phospholipid membranes drastically increases under the effect of some antibiotics produced by bacteria and fungi. Worthy of notice among pore-forming antibiotics are gramicidin and fungicidin (Nystatin).

The import of substances into root cells is stimulated by that many ions in the cytoplasm become rapidly involved in biosynthetic processes and the concentration of ions in the cells rapidly decreases as a result of formation of organic substances.

Two systems of ion transport have been established. The first system is more selective; as a rule, it functions under natural conditions at a low external ion concentration (less than 1 mM). The increasing concentration of ions in the external solution causes rapid saturation of the first system, and this is where the second, less selective system takes

over, characterized by less pronounced ion affinity (see Fig. 2.13).

The first system is believed to be localized in the plasmalemma. As regards the second system, it is presumably localized in the plasmalemma or, more probably, in the tonoplast.

Carriers may be protein globules having a diameter exceeding the thickness of the cell membrane. In this case, rotation of a globule about its axis ensures transfer of ions from the outer side of the membrane onto the inner one. Such transport of ions is exemplified by the ion pump which is essentially transfer ATPase. ATPases owe their name to their capacity to catalyze the hydrolysis of adenosine triphosphate (ATP). The energy released in the process is used to transport substances, and transfer ATPase is reversibly phosphorylated. The molecular weight of transfer ATPases ranges from 200 to 700 thousand. The phosphorylation and dephosphorylation of transfer ATPase are accompanied by fixation and liberation of ions with simultaneous conformational changes of the ATPase molecules, which enable the ions to be imported into the cell (Fig. 2.14).

By conformational changes are meant changes in the spatial configuration of the protein molecule, involving disulphide, hydrogen, and ionic bonds as well as hydrophobic interactions of the polypeptide chain.

The ion pump is intended to maintain a constant ionic composition in the cell in compensation for the possible losses due to metabolic reactions and diffusion.

Thus, active transport of ions into cells is assisted by special ATPases through a mechanism known as ion pump.

The transfer ATPases responsible for functioning of the potassium-sodium pump, calling for the presence of Mg^{2+} and additionally activated by Na^+ and K^+ ions, were discovered in animal cells in 1957. The first report about the presence of sodium ATPase in plant cells was published in 1964. At present, the existence of a potassium-sodium transfer ATPase in plants may be considered as definitely proved. This specific enzyme pumps Na^+ ions out of cells and K^+ ions into them. It may be assumed that there also exists a proton pump removing H^+ ions from cells which become negatively charged. The theory of ion pumps has been around

for quite some time, and it used to be believed that there must be as many pumps as ions transported into and from cells. Yet the currently known mechanism of translocation of various ions suggests that only sodium and hydrogen ion (proton) pumps are in existence.

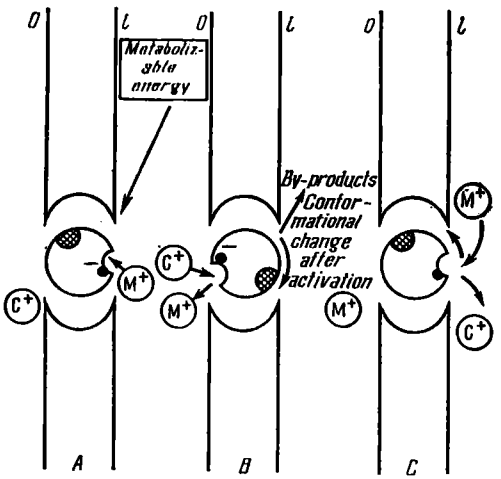


Fig. 2.14: Hypothetical mechanism of an electrically neutral ion pump enabling ion transfer against the electrochemical gradient. 'A' stands for activation. The active portion consumes metabolizable energy and an M^+ cation is attached to the exchange site. 'B'indicates reorientation. In the activated pump, the exchange site changes its orientation and becomes oriented towards the external medium. Under these new conditions, the strength of its electric field changes so that cation C^+ is preferably attached to it. 'C' stands for relaxation or, in other words, transition from an activated into inactivated state. The initial orientation of the pump is restored: the exchange site together with the C^+ cation becomes oriented inwards. Here, M^+ is preferably attached to the exchange site, while C^+ is released; o—outer medium; i—internal medium

The energy of hydrogen or sodium ion transport may assist in the import of certain ions and export of some or other anions.

The translocation of substances against the electrochemical gradient requires a steady source of energy, and the demand in it may arise at different stages of nutrient transport.

It is precisely the energy requirement that accounts for the close relationship between nutrient uptake by plants and the metabolic processes of respiration and photosynthesis, yielding high-energy compounds.

The carrier-assisted ion transport rate is determined by that of the carrier turnover which depends on temperature, oxygen concentration, presence of an inhibitor, and other factors, as well as by the number of the carrier-localizing sites exhibiting ion affinity and occupation of the active sites, which varies with the concentration of translocated and other ions in the medium.

The wide popularity of the carrier theory stems from the fact that it accounts for the selectivity of uptake, interaction between ions, and inhibition of the processes by some antibiotics. It should be pointed out that there apparently exists a mechanism controlling the import of substances into cells on the feedback principle. For example, according to Pitman, the maximum ion content in root cells is 80 to 90 meq/g fw. In various plants, this quantity is independent of the ion concentration in solution and is attained after 10 to 15 h of uptake from a 10-mM solution, 20 h from a 1-mM solution, and 36 h from a 0.1-mM solution.

Some substances may be transported across the membrane with the aid of low-molecular fat-soluble carriers. When such a carrier has captured a passing ion, it easily penetrates through the phospholipid membrane, being dissolved in it and freeing the ion inside the cell. The import of substances into the cell across membranes may proceed via pores in the plasmalemma. These pores, whose presence is yet to be proved by electron-microscope examinations, may exist temporarily or permanently. Obviously, the pore diameter must be 0.5 to 0.8 nm (for comparison, the diameter of a K^+ ion with the hydrate envelope equals 0.34 nm). According to the pore theory, substances soluble in water and insoluble in membranes may be transported through pores. Membrane proteins are responsible for the substrate specificity of transport.

Recently, plant cells were found to have single channels letting calcium through.

The transport of substances through hydrophilic channels or pores in the cell membrane depends on the channel

selectivity. It may involve a relay mechanism, that is, the ion or molecule of the passing substance is successively transferred from one carrier molecule to another. In this case, the carrier molecules become embedded in the membrane one after another and relay the ions or molecules captured by the outermost carrier molecule. If the carrier moves together with the ions imported into the cell, the translocation is said to proceed in a shuttle manner.

Simport and Antiport. Hydrogen ions are removed from the cell by a proton pump, which creates a certain concentration and electric gradient.

In the process, the cell medium is slightly alkalized. As a result of the alkalization, the carrier may transport protons back into the cell following the electrochemical gradient. But when a carrier does so, it must have affinity to some other species, such as an anion translocated into the cell. According to the terminology proposed by Mitchell, the active pumping of a proton and a "rider" (amino acid, sugar, phosphorus, etc.) into the cell is called simport. The opposite process, or antiport, implies pumping of a proton (H^+) from the cell with delivery into the latter of an ion with the same charge, such as K^+, to maintain the electroneutrality.

The import of nitrogen into plants proceeds much more easily than that of phosphorus. It should be borne in mind here that absolutely impermeable membranes simply do not exist. The NH_4^+ cation in the medium is at equilibrium $NH_4^+ \nearrow^{H^+}_{\searrow NH_3}$ and gives ammonia and hydrogen. The molecule of NH_3 enters the cell a thousand times faster than any other electrically neutral molecules with the exception of water. As it passes across the membrane, ammonia takes a proton from water to form ammonium NH_4^+ and hydroxyl OH^-:

$$NH_3 \longrightarrow NH_3 + H-OH = NH_4^+ + OH^-$$

$$NH_4^+ \nearrow^{OH^-}_{\searrow H^+}$$

What happens is alkalization of the cytoplasm, whereby pumping out of the proton and the operation of the proton

pump are impeded. On the other hand, alkalization facilitates the import of phosphorus.

Such anions as NO_3^-, CN^-, and I^- traverse the membrane more reluctantly than NH_4^+ cation. These ions are believed to pass across membranes a hundred to a thousand times more slowly than K^+ and NH_4^+. When in high concentrations, these anions may disrupt the hydrogen bonds of membranes and are therefore called chaotropic.

Evidence to the effect that nitrate passes easily across a membrane is provided by the following experiment. If added to the medium accommodating a liposome (a tiny droplet confined by an artificial bilayer membrane) are KNO_3 and valinomycin, the latter creates a potassium "hole", K^+ ions and NO_3^- anions start filling the liposome, and it swells rapidly. But if KCl is substituted for KNO_3, the membrane becomes impermeable to Cl^-. A very small amount of potassium will enter the liposome with the aid of valinomycin, the process will come to a halt as a result of the diffusion potential, and the liposome will swell no more.

The fastest substance to traverse membranes is water. For example, if two compartments are divided by a membrane and one of them is filled with labelled water, very soon equal quantities of labelled water will be found in both compartments.

Pinocytosis. Mechnikov discovered that leukocytes are capable of "swallowing" bacteria. Later, it was found that many cells can take up solid particles and droplets suspended in the surrounding medium. This phenomenon was termed phagocytosis when applied to ingestion of solid particles by cells and pinocytosis in the case of ingestion of liquid drops. Pinocytosis is one of the possible pathways of nutrient import into plants. First, the ingested particulate matter is adsorbed on the cell membrane, then the membrane invaginates, and its constricting edges eventually close. A pinocytic vesicle is thus formed, which is then detached from the outer membrane and migrates into the cell (Fig. 2.15). Here the membrane envelope of the vesicle is attacked by an enzyme, and the entrapped particles find themselves in the cytoplasm. The process of vesiculation and detachment of the vesicle from the outer membrane require energy which is provided in the form of ATP.

Disintegration of the pinocytic vesicle results from its fusion with the lysosome containing a number of hydrolases that split macromolecules.

It has been reported that pinocytosis is initiated over certain portions of membranes by appropriate substances adsorbed on their surfaces. There is evidence of reverse pinocytosis, i.e. a process allowing cells to expel out cer-

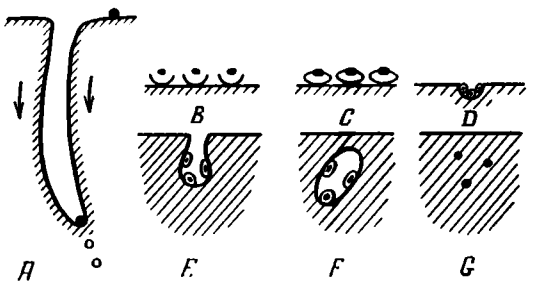


Fig. 2.15: Two possible pinocytosis mechanisms. According to the first mechanism (A), the membrane invaginates into the cell, forming a narrow duct. Small vesicles with the entrapped substance detach themselves from the end of the duct. In accordance with the second mechanism (B-G), the membrane portion that has adsorbed macromolecules (C) invaginates (D). The membrane edges at the invagination point close (E), and the resulting pinocytic vesicle is detached from the cell membrane (F). Inside the cell, the vesicle membranes are broken down by enzymes (G)

tain noxious substances while retaining other molecules floating freely in the cytoplasm.

In conclusion, it should be pointed out that, irrespective of the manner in which they traverse the plasmalemma, the molecules or ions imported into a cell from the external solution are almost never involved in metabolic reactions at the plasmalemma level and may proceed along the following routes after having entered the cell: (1) having undergone the cycle of metabolic transformations, the imported substances are incorporated into the organic compounds of the structural cell components; (2) excess ions are accumulated in root cell vacuoles, forming a pool, or translocated into the above-ground organs of plants via xylem vessels; and (3) ions may be exported from the plant organism back into the surrounding medium.

2.9 Effect of Environmental Conditions on Nutrient Uptake by Plants

The uptake of nutrients from the soil is an active physiological process associated with the vital activity not only of the root system, but also of the plant as a whole. Among the metabolic processes inherent in root cells, including growing ones, are respiration and synthesis of the substances (carriers) providing for transport of ions and, more specifically, import of inorganic nutrients.

The productivity of plants and uptake of macro and micronutrients by them are directly dependent on the inorganic nutrient content in the soil.

Nutrients may be present in the soil solution (various inorganic and organic soluble compounds), in the organic matter of the soil (crop residues, humus substances, and microorganisms), and in the solid inorganic phase of the soil.

All soluble and exchangeable forms of nutrients are readily available to plants. The rest of the nutrients are not directly available and can be taken up only after conversion into a more available form (as a result of breakdown of the primary minerals in the course of weathering, mineralization of the organic matter, and other processes). It should be noted that under the effect of environmental factors some of the macro- and micronutrients present in the soil can pass into an unavailable form (in the case of changing reaction of the medium, stronger microbiological fixation of the nutrients, and so on), which accounts for their reduced uptake by plants. Plants themselves produce a tangible effect on the availability of various nutrients. The reaction of the medium, changing under the effect of various substances exuded by plants, is conducive to transition of some unavailable soil nutrients into an available form.

The uptake of nutrients by plants depends on plant species and soil properties, including the potential fertility level associated, primarily, with the content of the organic matter and mineralogical composition of the soil, its texture, temperature, moisture content, aeration, reaction and concentration of the soil solution, illumination, and other factors.

For example, during the night hours the uptake rate of potassium, calcium, and phosphorus decreases 1.5 to 3 times. Naturally, the responsible factors in this case include not only darkness, but also different soil and air temperatures, lower transpiration rate, cessation of photosynthesis, and so on.

The genetic characteristics of soils and their texture, or grain size distribution, determine the possible yields of agricultural crops on these soils (Table 2.9).

Table 2.9. Highest Possible Yields (in centners per hectare) **of Various Crops Depending on Soil Texture** *

Crops	Loam	Sandy loam and sand on moraine	Sandy loam on sand	Sand
Winter rye	50-55	45-50	40-45	30-35
Winter wheat	55-60	50-55	45-50	35-40
Barley	60-75	55-65	50-60	40-50
Oat	50-60	45-55	40-45	30-40
Potato	400-500	350-450	300-400	250-300
Sugar beet	500-600	450-500	400-450	300-350
Flax (fibre)	18-22	17-19	—	—

* The term 'highest possible' yield as used here applies to definite crop varieties and cultivation practices. In reality, the maximum potential yields of crops are several times higher.

Fertilizer application procedures can be steadily improved with knowledge of not only soil and fertilizer properties, but also the constantly changing nutrient requirements of plants, the mechanism of nutrient uptake, and other factors related to plant physiology and biochemistry, soil science, and other disciplines.

Effect of Nutrient Solution Concentration on Plant Nutrition. The soil solution concentration and the ratio of plant nutrients are essentially environmental factors. If the nutrient solution concentration is too low, plants grow less intensively and suffer from inorganic nutrient deficiency. A high concentration of the nutrient solution also adversely affects plant growth and may inhibit it.

The optimal nutrient solution concentration, that is, ensuring highest productivity of plants under a given set

of conditions, varies widely at different stages of ontogeny for one species, and even variety.

The root system of plants is capable of taking up nutrients from highly dilute solutions (0.01-0.05%), especially if their concentration is maintained at this level. Under natural conditions, the concentration of nonsaline soil solutions varies from 0.02 to 0.2 per cent.

Inorganic nutrients are most actively taken up by plants only when present at a particular concentration in the soil solution. Nutrient ions are more readily taken up from solutions of moderately high concentrations, while water is best absorbed by a root system located in a nonfertilized part of soil. This is an important consideration in evaluating localized, or spot, application of fertilizers.

The osmotic pressure of the soil solution increases with its salt concentration, whereby the uptake of water and nutrients is hindered.

Plants are especially sensitive to excess increases in the nutrient solution concentration when they are young. Individual crops cannot tolerate nutrient solution concentrations increasing beyond a certain limit (when they are within the range of optimal concentrations for growth and development of other crops) (Table 2.10).

As can be seen from the tabulated data, an increase in the nutrient solution concentration up to 15.7-25.9 mM/litre

Table 2.10. Effect of Nutrient Solution Concentration on the Growth and Yield of Cucumber (from Zhurbitsky)

Nutrient solution concentration		Weight of 10 26-day-old plants		Harvested green material		Harvested fruits		Fruit percentage of green material
g/litre	mM/litre	g	%	g	%	g	%	
Water	—	10	—	—	—	0	—	—
0.41	2.9	138	53.7	145	60.5	27	8.6	19
0.74	5.4	175	68.0	152	63.5	99	31.6	65
2.13	15.7	265	103.0	230	96.0	174	55.5	76
3.56	25.9	257	100.0	240	100.0	314	100.0	130
4.96	36.2	188	72.8	205	85.5	130	41.5	65
6.93	46.5	177	69.0	110	46.0	53	16.9	48

enhances plant development, the highest yield being obtained at a concentration of 25.9 mM/litre.

Higher nutrient solution concentrations, i.e. from 36.2 to 46.5 mM/litre, produce a pronounced negative effect. At these concentrations, month-old plants at the flowering stage exhibit dried edges of median and lower leaves with dried and brown interveinal portions.

The different sensitivity of some plants to nutrient concentrations and their response to inorganic nutrient concentrations at different stages of ontogeny must be taken into consideration in formulating fertilizer systems for farm crops.

Ratio Between Macro- and Micronutrients in the Nutrient Medium and Their Uptake by Plants. Plant nutrition must be evaluated quantitatively, that is, in terms of the nutrient uptake trend during the vegetation period, and qualitatively, in terms of the ratio between the nutrients taken up by plants at different developmental stages.

Experiments have shown that a major factor of inorganic nutrient uptake is the ratio of ions in the medium. Each species requires a certain nutrient ratio varying throughout the vegetation period, which determines the productivity of crops and their quality. When nutrients are absorbed by the root, the diameter of ions in the hydrated state is a matter of importance. Accordingly, univalent cations must enter root cells at a faster rate than bi- and multivalent ones. However, the decisive role is played by the specific features of the absorbing system. For example, potassium enters roots faster than rubidium and cesium, although the diameter of hydrated ions of the latter two elements is smaller than that of potassium ions. Similarly, the uptake of chlorine ions is faster than that of iodine and bromine ions. Note that the interrelationships among ions in the nutrient medium are not confined to the above pattern.

There is a wealth of experimental evidence testifying to the effect of the nutrient ratio in the external medium on the uptake and accumulation of nutrients by plants.

The question whether the uptake of nutrients depends on their concentration in the external solution is yet to be answered. Our experiments have demonstrated a close relationship between the uptake of cobalt by plants and its

concentration in the solution. It has been established that, when plants are nourished from a solution containing a mixture of nutrients, especially soil solution, it is not the concentration of nutrients that is decisive but their ratio and mutual influence.

Changes in the nutrient content elicit numerous responses from plants. In particular, acute deficiency of any nutrient

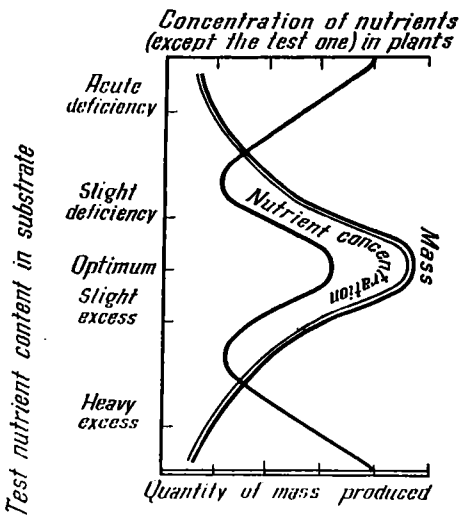


Fig. 2.16: Produced mass versus nutrient concentration in plants at different contents of the nutrient of interest in the substrate

may cause plants to respond by taking up greater amounts of others. A slight excess of a macronutrient, when the plant is not yet in mortal danger, sharply decreases the import of other nutrients. Excess of some nutrients may be eliminated by introduction of others. For instance, in experiments with lettuce and barley, a slight excess of Mg was offset by N, excess amounts of Cu were neutralized by Ca and Fe, and Zn was counterbalanced by Mg.

The concentration of nutrients in plant tissues features three maxima: at an optimal uptake rate, acute deficiency, and overabundance of the nutrient under examination in the substrate (Fig. 2.16).

Plants function normally at a strictly defined ratio of cations and anions in the external medium. This fact pro-

vides the theoretical basis of nutrient mixture formulation. Another fact of importance is the antagonism of ions during their uptake, known as physicochemical antagonism, residing in that similarly charged ions interfere with one another as they try to enter a living cell.

Exchange adsorption, as the first step of nutrient uptake, oriented towards the outer side of the membrane (plasmalemma) of a plant's root, allows this phenomenon to be regarded as competition among ions for their penetration by way of exchange into the Donnan space.

At subsequent steps of nutrient uptake, the interaction of nutrients becomes more complicated. Here, mere competition among similarly charged ions cannot materially affect this process. At the second step of nutrient uptake, the ion antagonism seems to be possible only if the different ions have similar chemical properties and the capacity to form covalent bonds with the same metabolites (carriers).

It should also be noted that the import of some deficient macro- and micronutrients activates certain metabolic reactions with the result that the overall physiological state of the plant is improved and the requirements for other nutrients increase. Apparently, one of the mechanisms of the so-called synergism often observed when a nutrient is added to the medium may be regarded as increased import of other ions into the plant as a consequence of promoted metabolic reactions.

The growth of above-ground organs and development of the root system depend on the physiological balance of the nutrient solution.

A solution is said to be physiologically balanced if the constituent nutrients are present in ratios ensuring their most effective utilization by plants.

In a physiologically balanced solution, all nutrient salts necessary for normal growth and development of a plant must be in optimal concentrations and ratios.

A single-salt solution cannot meet the nutrient requirements of a plant even over a short period of time because it is not physiologically balanced.

Note that various salts in the form of a single-salt solution produce different effects on plants (Table 2.11).

Table 2.11. Growth of Wheat Roots Depending on the Nutrient Solution Composition

Salt	Length increments of roots over a 40-day period (mm)
NaCl	59
KCl	68
$MgCl_2$	7
$CaCl_2$	70
$NaCl+KCl+CaCl_2$	324

An important factor in studying the nutrient uptake pattern is duration of the experiment in view of the fact that prolonged exposures bring about pronounced changes in the physiological state of the test plants, particularly in absorbing capacity of the root system.

Elucidation of the causes and pattern of changes in the uptake of nutrients, depending on their composition and concentration in the medium, is of great theoretical and practical importance.

The presence of nitrogen, phosphorus, and potassium in the nutrient medium determines to a great extent the plant growth rate and uptake of other inorganic nutrients by plants. Increased uptake of nitrogen enhances the import of P, K, Ca, Mg, Cu, Fe, Mn, and Zn into plants. The effect of nitrogen on the uptake of the above nutrients is reversed by its excess amounts and depends on the form in which it is taken up.

Excess phosphorus reduces the import of copper, iron, and manganese. In the presence of phosphates, plants take up less zinc.

As regards the effect of potassium, there is evidence that it reduces the import of calcium, magnesium, and some other nutrients into plants.

The better the supply of the basic nutrients (NPK) to plants, the more micronutrients they need. Micronutrients, in turn, play an important role in enhancing the effectiveness of the macronutrients taken up by plants.

For example, in experiments, the import of nitrogen into plants was reduced at iron, manganese, and zinc deficiency

and was independent of the import of copper, boron, and chlorine. Under a different set of conditions, the accumulation of nitrogen in plants perceptibly increased when copper and boron were introduced. There are indications that molybdenum substantially improves the utilization of nitrogen from fertilizers and soil. Our observations show that utilization of nitrogen is improved not only by molybdenum but also by cobalt. There are reports that the uptake of phosphorus by plants increased in the presence of copper, zinc, calcium, and molybdenum, but magnesium and iron produced an opposite effect. Less potassium was taken up in the presence of copper, manganese, nickel, zinc, molybdenum, iron, and boron but more in the presence of chlorine.

The literature contains many examples of ion antagonism and synergism.

For example, Fe and Ca, Al and Na, Fe and Zn, Mn and Zn, Cu and Zn, Zn and Fe, Mn, Cu, Mo have been found to be antagonistic. On the other hand, synergism has been established between S and Mn, Zn, Cu and Co, B, Zn, Co, Mo and Mn, Mo and Cu, Cu and Mn, Ca and Co.

Thus, the same ions may promote or inhibit the uptake of others, depending on the prevailing conditions. Whether the uptake of macro- and micronutrients is governed by antagonism or synergism may depend on the reaction of the medium, content of other inorganic nutrients in the medium and plants, their ratio, plant species, ambient temperature, and other factors.

Depending on the above conditions, antagonism may give way to synergism and vice versa.

The uptake of necessary inorganic nutrients follows a definite pattern. Deviations in the content of a particular nutrient by 30 to 100 per cent from its optimal concentration in the substrate lead to different rates of uptake of other nutrients, and if the content of this nutrient, which was deficient, increases, the uptake of others is facilitated (synergism), whereas its excess produces an inhibiting effect (antagonism).

When the departure from the optimal content in any direction is substantial (100 and more times), the relative content of other nutrients increases; at the same time, the absolute rate of their import decreases because of the consid-

erably slowed plant growth. However, a small decrease in the content of a nutrient in the substrate, as compared to the optimum, restricts the uptake of other nutrients.

The data concerning the interaction of anions during their uptake are more scant than those concerning cations. Just as with cations, the interaction between anions has been found to involve both antagonism and synergism. According to Potapov, when NO_3^-, PO_4^{3-}, and SO_4^{2-} anions interact with the absorbing surface of the root, no competition arises among them; they do not interfere with one another during primary fixation. Anions may compete only if they exhibit related chemical properties (e.g. SO_4^{2-} and SeO_4^{2-}). There is no competition between NO_3, PO_4^3, and SO_4^{2-}, on the one hand, and halogens, on the other, as they enter a living cell, owing to their different chemical properties. The halogens taken up by the root system were found to be in distinct antagonism.

The total content of individual nutrients in soils differs widely. According to G. Ya. Rinks, the content of calcium in soils may vary by a factor of 1310; the contents of phosphorus, magnesium, iron, copper, manganese, cobalt, and boron may vary 100- to 300-fold. Similar variations are observed in the same nutrients dissolved in 1 *N* hydrochloric acid: the content of manganese varies by a factor of 70, while that of iron, by a factor of 1420. The least variations have been found in nitrogen and potassium contents in the soil (about ten-fold).

The root system of plants responds differently to various nutrients. The deficient ones are the first to be taken up, while the ions not needed by plants may be exported back into the soil. Cell vacuoles tend to compensate for the variations in the external concentrations of nutrients. They irreversibly retain unnecessary nutrients and may accumulate nutrients whose content in the soil around the root is high at that moment.

Of paramount importance for yields is the capacity of plants to utilize inorganic nutrients a number of times.

In assessing the supply of nutrients to plants, it should be borne in mind that they can be partially reutilized, for example, when they are exported from leaves into reproductive organs. However, such nutrients as calcium, iron,

manganese, boron, copper, and zinc do not lend themselves to reutilization; sulphur is partially reutilized as a constituent of organic compounds. Nitrogen, phosphorus, potassium, and magnesium can be reutilized many times.

The multiply utilized nutrients become deficient first in old leaves. Older organs of plants also display more pronounced signs of excess of nutrients that cannot be reutilized and that are overabundant in the external medium.

There is a wealth of data concerning inorganic nutrient uptake by plants, which suggest that the process of nutrition depends on adequate supply of all elements. As a rule, an increasing concentration of any nutrient in the medium not only leads to an increase in its content in plants, but also affects that of other nutrients.

The content of inorganic nutrients determines their interaction, giving rise to rapid transitions from antagonism to synergism and vice versa. A drop in temperature or reduced illumination enhances the effect of excess nutrients, while higher humidity mitigates their negative influence. For example, the content of nitrates in vegetables increases when they are grown in hothouses in winter under subdued light.

An increase in nitrate content may be brought about by many factors, including higher application rates of nitrogen fertilizers. For example, increasing rates of nitrogen fertilizers in experiments with head lettuce not only add to the weight of the head, but also lead to accumulation of greater amounts of nitrates in it (Table 2.12).

Table 2.12. Effect of Nitrogen Fertilizer Rates on the Weight of Head Lettuce and the Nitrate Content in It

Nitrogen rate (kg/ha)	Head weight (g)	N (NO_3) content	
		mg/head	mg/kg
0	79	45	569
50	93	63	677
100	149	129	866
200	160	200	1250
400	169	211	1248

The content of nitrates in crops can be reduced substantially by growing them under conditions of fully balanced inorganic nutrition. Apart from enhancing the yield, this measure also greatly improves the crop quality (Table 2.13).

Table 2.13. Quality of Cotton Fibre Over Many Years of Experimentation with Potassium Fertilizers

N : P_2O_5 : K_2O rate (kg/ha)	Sympodial branches	Metric count	Maturity factor	Strength (g)	Breaking length (km)	Commercial grade
150 : 100 : 0	4-6	5420	2.07	4.7	25.6	1
	7-9	5570	2.01	4.5	25.0	1
	10-12	5870	1.95	4.3	25.0	2
150 : 100 : 100	4-6	5310	2.11	4.9	25.9	0
	7-9	5480	2.05	4.6	25.2	1
	10-12	5580	2.00	4.5	25.2	1
150 : 100 : 150	4-6	5220	2.16	5.0	26.0	0
	7-9	5250	2.14	5.0	26.2	0
	10-12	5300	2.12	4.9	26.1	0

Soil Moisture. Sufficient amounts of moisture in the soil are a prerequisite for normal development of plants and a major factor of their nutrition.

When the soil contains normal amounts of inorganic nutrients, there is no direct relationship between the rate of their uptake and that of transpiration. However, when macro- and micronutrients are present in excess amounts, their uptake by plants increases with the transpiration rate.

The effect of soil moisture on nutrient uptake is determined primarily by the following physiological and physical factors:

1. Improvement of the general physiological state of plants in view of the fact that normal hydration of their tissues promotes photosynthesis, protein biosynthesis, and some other metabolic processes on which the uptake of nutrients is strongly dependent.

2. Improved development and arrangement of roots at normal moisture contents in the soil, hence increased overall absorbing capacity of the roots.

3. Water being a universal medium for ion diffusion from the soil solution and absorbing complex of the soil towards root hairs.

These factors are associated with the positive effect of soil moisture on the uptake of macro- and micronutrients by plants.

Experiments have shown that the overall uptake of N, P, K, Ca, Mg, Zn, Cu, Mn, Co, Fe, Mo, and B increases at optimal moisture content in the soil.

When moisture is deficient, the nutrient uptake becomes difficult.

The negative effect of excess moisture in the soil on nutrient uptake may manifest itself in a disproportional increase in the availability of some ions, particularly ferrous and manganous salts whose accumulation in the plant may lead to a toxic concentration.

Moisture deficiency upsets the functioning of enzyme systems, intensifies hydrolysis and degradation of organic substances, sharply reduces the photosynthetic rate, and brings plant growth to a halt.

On a hot summer day, a plant transpires within an hour almost the same amount of water as is contained in the entire plant.

Water is transpired primarily through stomata. But the latter also let in CO_2 indispensable for photosynthesis.

Even the immense absorbing surface of the root system cannot provide for the necessary amounts of water for transpiration around noon on a hot summer day if the soil is deficient in moisture. What is known as midday depression of photosynthesis occurs, i.e. the stomata close, and plants stop transpiring water, whereby the uptake of carbon dioxide also discontinues.

Note that only about 0.2 per cent of the water imbibed by roots is utilized in building the plant body, the rest, or more than 99 per cent, is lost by transpiration.

The water requirements to build a unit of dry matter are considerably lowered under conditions of adequate inorganic nutrient supply to plants (Table 2.14).

In Pryanishnikov's fertilizer experiments, the water requirements per unit dry matter were reduced by 36.5 per cent at a low moisture content in the soil and by 20 per cent at a high moisture content.

The transpiration of water by plants is minimal at high relative air humidity. At the same time, high air humidity

Table 2.14. Water Requirements to Build a Unit of Dry Matter

Experimental conditions	Wheat	Flax
Without fertilizers	800	1092
N	917	1198
NP	545	1000
NPK	480	787

Table 2.15. Effect of Air Humidity on Transpiration of Water by Sunflower, Its Yield and Nutrient Uptake (Water Cultures)

Relative air humidity	Transpiration rate (litre)	Yield of dry matter (g)	Uptake rate (mg/litre of transpired water)		
			Ca	K	P
Low	42.3	65.4	32.0	133	13.2
High	32.8	70.4	37.3	160	15.9

intensifies plant growth and nutrient uptake (Table 2.15).

It should be pointed out that cultivation practices produce a tangible effect on the moisture content in soils. For example, the moisture content in experiments with chemical fallow, that is, involving multiple treatment with herbicides, increased four-fold as compared with that in a mechanically treated fallow plot.

The restrictive effect of soil moisture on yields of farm crops is dependent on the availability of nutrients. It is known that even when experiments are carried out in a water culture, a high concentration of the nutrient solution causes physiological dryness.

High fertilizer rates necessitate sufficient moisture contents in the soil, and under dry conditions special attention must be given to the rates of nitrogen and potassium fertilizers "responsible" for the total ionic strength of the solution.

Better nutrition conditions are conducive to a more efficient utilization of moisture; adequate moisture content, in turn, ensures yield increase due to fertilizers, as has been demonstrated by application of fertilizers on irrigated lands.

Aeration and Plant Nutrition. The aeration of soil and nutrient solutions drastically affects the nutrient uptake rate. Hogland was the first to demonstrate it. His experiments with aeration of nutrient media have given new insights into the physiology of inorganic plant nutrition.

The content of oxygen and carbon dioxide in the medium around roots varies widely. Under partially anaerobic conditions, the supply of oxygen to absorbing cells is worsened, and the carbon dioxide content increases. The relationship between the absorbing activity of the root system and aerobic respiration determines nutrient uptake as a function of oxygen supply. One of the basic requirements to growing plants in a water culture is aeration of the nutrient solution. The role of soil structure in inorganic nutrition is also associated to a certain degree with improved gas exchange in roots.

Experiments have made it possible to establish the effect of aeration on the uptake of various nutrients by plants. They have shown that plants respond differently to aeration while taking up nutrients, their sensitivity increasing thus: $K < Ca < Mg < N < P$.

Just as with roots of whole plants, cultivation of isolated roots has been found to involve maximal inorganic nutrient uptake at an oxygen concentration of two to three per cent. Increasing the oxygen concentration further to 100 per cent does not entail any increase in the salt uptake rate. Other experiments have shown that the uptake of phosphates by barley roots is independent of partial oxygen pressure within 3 to 100 per cent, provided the total gas pressure is maintained equal to 1.01×10^5 Pa.

Optimal aeration conditions and air temperatures of the soil (or any other nutrient medium) produce a perceptible effect on the uptake of inorganic nutrients (Table 2.16).

Roots of most farm crops can perform their absorbing functions only under conditions of adequate aeration. The above-mentioned optimal oxygen concentration of about 3 per cent is not the same for all plants. The ambient gas composition in areas where plants develop normally (industrial regions, alpine areas, different aeration conditions in various soils, etc.) is known to vary widely. It should be borne in mind, however, that insufficient aeration of the

Table 2.16. Effect of Temperature and Aeration on Tomato Yields and Nutrition

Solution temperature (°C)	Aeration	Yield (kg)	Uptake rate (meq per plant)				
			NO_3^-	$H_2PO_4^-$	K^+	Ca^{2+}	Mg^{2+}
14-20	normal	7	776	115	506	329	141
20-23	normal	8	854	143	600	393	143
14-20	intensified	10	1074	160	738	445	197

root system significantly upsets the normal course of absorbing activities of roots.

The oxygen content in the soil determines the redox potential of the substances or systems of substances present in it. For example, in the case of cations, compounds of metals with the lowest possible valence (Fe^{2+}, Mn^{2+}, etc.) are more readily soluble and mobile as a rule. As regards anions, their mobility and, consequently, uptake by plants increase with the valence of the constituent element (Mo^{6+}, Cr^{6+}, V^{5+}).

There is evidence that carbon dioxide inhibits the uptake of nitrates, phosphates, and ammonium ion by the root system. Blowing carbon dioxide through the nutrient solution has been found to inhibit the absorbing activity of maize, rice, and wheat roots.

Aeration of the soil exerts a strong influence on soil microorganisms and the processes of nutrient conversion in the soil associated with their vital activities.

Heat and Plant Nutrition. All kinds of vital activity of plants are possible only within a definite temperature range. The optimal temperature for germination of barley seeds is 20 °C; for oat, wheat, and rye, it is 25 °C and, accordingly, 28 °C for tobacco, 32 to 35 °C for maize and sorghum, and 33 to 35 °C for cucumbers and pumpkin. For most plants grown under sufficient illumination and with adequate water supply, the favourable air temperature ranges from 15 to 30 °C. The optimal temperature for uptake of nitrogen and phosphorus by grain crops is normally 23 to 25 °C. However,

the protein content in the kernels of wheat may increase appreciably when the temperature rises to 35 °C. Apparently, under favourable moisture conditions (60% of total moisture capacity), an increase in soil temperature promotes mobilization of nitrogen, which can be seen in its uptake by plants and the content of proteinaceous substances.

It has long been noticed that the content of protein in wheat is higher in the south-eastern parts of the USSR as opposed to the north-western ones. This is consistent with the arid climate and elevated temperatures during the vegetation of plants in the south-eastern regions. Castor bean, soybean, kidney bean, cotton, and other southern crops take up nutrients more readily at 30 to 35 °C.

It is known that roots grow well at soil temperatures slightly lower than the air temperature for growth of the aboveground organs. However, the difference between the two must be small. The minimal soil temperature for sprouting of hemp is 2 to 3 °C, while for spring cereals and pea it is 4 to 5 °C. Minimal temperatures of the same order of magnitude are sufficient for formation of vegetative organs.

The formation of reproductive organs proceeds best at the following minimal temperatures: 10 to 12 °C for hemp, spring cereals, and pea; 12 to 15 °C for buckwheat, sunflower, maize, and millet; 13 to 20 °C for rice and cotton. During fruit bearing, the temperatures of 10 to 12 °C are quite sufficient for most crops and 15 to 20 °C for rice and cotton.

Temperature conditions are important not only for germination of seeds and sprouting, but also for uptake of nutrients by plants.

It has been established that ammonia nitrogen can be taken up at lower temperatures as compared to nitrate nitrogen.

Roots of wheat sprouts have been found to take up undiminished amounts of potassium but much lower ones of nitrogen, phosphorus, calcium, and sulphur when the temperature drops to 5-7 °C.

Each plant species and even variety is characterized by temperatures corresponding to most active uptake of particular nutrients (Fig. 2.17).

At low temperatures (10-11 °C), plants have difficulties with taking up phosphorus. The uptake of nitrate nitrogen

slows down at temperatures below 5-6 °C. Low temperatures also adversely affect the uptake of potassium.

Thus, under optimal inorganic nutrition conditions, the temperature of 5-6 °C is critical for uptake of the basic nutrients.

Low temperatures make it difficult for inorganic nitrogen compounds to be involved in synthesizing processes. Temperatures below 10 °C are believed to inhibit the uptake of all inorganic nutrients via roots.

The inorganic nutrient uptake rate increases with temperature up to a certain limit, this increase varying from one plant to another.

The reduced uptake of salts at temperatures ranging from 40 to 50 °C seems to be caused by inactivation of the enzyme systems participating in ion uptake. At low temperatures, the uptake of inorganic nutrients is reduced to a minimum as a result of variations in chemical reaction rates and the effect of these temperatures on the absorbing organs.

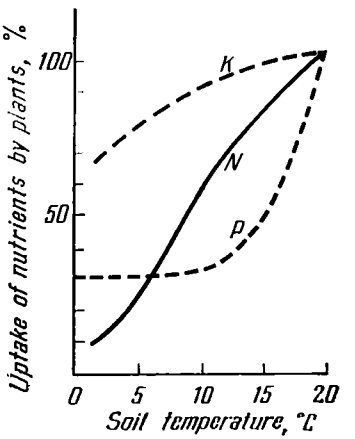


Fig. 2.17: Effect of medium temperature on nutrient uptake (% of uptake at 20 °C)

Light. Illumination of plants and their inorganic nutrient uptake are closely related just as any other factors of life. Plants live in two media, soil and air, which are characterized by constant variations in the environmental conditions: the day-night cycle, changes in humidity, temperature, content of available nutrients, and illumination intensity.

In the course of their evolution, plants have developed a capacity to respond to the varying environmental conditions and, thereby, to grow and develop normally. During photosynthesis, plants assimilate the energy of light, this event marking the onset of the energy exchange between plants and the environment.

Plants start vigorously taking up inorganic nutrients with the first rays of sunlight. Shading reduces not only the photosynthetic rate, but also the uptake of nutrients via roots. When plants are kept in the dark for a long period of time, the import of inorganic nutrients stops completely. This can be explained by accumulation, during photosynthesis, of organic substances utilized in respiration.

Shading of plants eventually brings the respiration process to a halt. Thus, the effect of light on nutrient uptake manifests itself in that plants photosynthesize substances necessary for the subsequent metabolic reactions of the absorbed ions and store energy.

Effect of Soil Reaction on Plants. Soil reaction (acidity or alkalinity) depends on the ratio of H^+ and OH^- ions in the soil solution. It is expressed as a concentration of hydrogen ions, in the form of the negative logarithm of 10, and denoted pH*.

Soil reaction is of great physiological importance for all plant organisms. Variations in the pH value of the soil, induced by liming with the result that hydrogen ions are replaced by calcium, influence the capacity of plants to utilize certain nutrients, which, in turn, affects many metabolic processes. As is known, calcium slows down the import of H^+ ions into plants and the latter become tolerant, at an increased calcium content, to a more acidic reaction of the soil (Table 2.17).

The effect of soil reaction on plant organisms may be direct or indirect. In the latter case, the pH of the medium

Table 2.17. Effect of Calcium Chloride on the Growth of Wheat Roots at Different pH Values of the Solution

Experimental conditions	Average root length (mm) at pH				
	5.3	4.9	4.7	4.3	4.0
Without $CaCl_2$	25	29	24	3	0
With $CaCl_2$	64	64	70	67	48

* For more detail on pH of the medium, see p. 159.

affects not the plant itself but the conditions on which its normal state is dependent. These conditions include, primarily, the effect of pH on the availability of inorganic nutrients for plants, acquisition of toxic properties by some nutrients when they are present in high concentrations, and so on. In an acidic medium, the amount of available forms of iron, manganese, cobalt, and copper increases, while that of available forms of nitrogen, phoshorus, molybdenum, and vanadium decreases.

The pH of the nutrient medium is a major factor determining the uptake of inorganic nutrients by plants (Table 2.18).

Table 2.18. Effect of Solution pH on Ion Uptake by Plants

Plants	Solution pH	Uptake (mg/h) from $(NH_4)_2HPO_4$	
		NH_4^+	HPO_4^{2-}
Fodder legumes	4.8	0.23	1.11
	6.6	0.89	0.13
	7.4	1.26	0.06
Wheat	5.3	1.40	0.92
	6.7	1.86	0.28
	7.3	2.26	0.10

It is well known that H^+ ions are predominant in an acidic solution and that an increase in the solution acidity facilitates the influx of anions. The uptake of cations is intensified, as a rule, when the solution is alkalified and OH^- ions become predominant. For example, the uptake of NH_4^+ is better at neutral pH values, while that of NO_3^- improves when pH shifts towards more acidic values. In soil cultures, this pattern is not always observed because the soil is a highly complex medium in which the availability of nutrients to plants is to a great extent dependent on their mobility. The concentration of hydrogen ions in the external medium is crucial for phosphate uptake in view of the fact that gradual alkalization of the medium causes the univalent form of phosphates ($H_2PO_4^-$), which is predominant in the soil, to convert first into the bivalent (HPO_4^{2-}) and then trivalent

(PO_4^{3-}) form. The growth of some plants may be inhibited at alkaline pH values since less phosphates are available under these conditions.

Pryanishnikov's experiments indicate that pH 7.0 is optimal for ammonia nutrition of sugar beet, while pH 5.5 is optimal for nitrate nutrition. Analysis of the test plants has revealed that leaves of the plants developing at acidic pH and with ammonia nutrition contain less calcium (because excess H^+ and NH_4^+ in the solution hindered the import of calcium into the plants). The negative effect of hydrogen ions is more pronounced at small quantities of other cations, especially calcium. Proceeding from these findings, Pryanishnikov succeeded in intensifying the development of sugar beet plants at pH 5.5, grown with ammonium supply, by introducing increased amounts of calcium into the nutrient solution.

Increased magnesium and potassium contents in the solution can produce a similar but less pronounced effect.

The influence of the medium pH on plants differs in intensity depending on many other factors. Plants are especially susceptible to it during the initial stage of growth. For example, a shift of the pH towards acidic values (pH 3.5) within the period of 40 to 60 days after sprouting fails to produce any appreciable effect on the yield of barley, although the same shift within the first 20 days and during the entire vegetation period sharply reduces the yield (Table 2.19).

High acidity adversely affects plants not only at a low content of calcium and some other ions in the soil, but also

Table 2.19. Solution pH and Barley Yield (g/pot)

pH variations during the vegetation period	Straw	Grain
pH 7.0 throughout the vegetation period	28.4	19.5
pH 3.5 throughout the vegetation period	6.4	1.5
pH 3.5 within the first 20 days, followed by pH 7.0	17.1	1.4
pH 3.5 within the period of 40 to 60 days after sprouting, followed by pH 7.0 for the rest of the vegetation period	26.1	17.5

in the case of insufficient illumination resulting in a decreased photosynthetic rate and deficiency of assimilates for certain metabolic processes, including import of inorganic nutrients and their involvement in metabolism. The effect of high acidity of the medium is enhanced by many other negative factors. For example, as has been shown by the experiments conducted at the department of agricultural chemistry of Moscow State University, the acidic pH with excess moisture causes a greater decrease in yield than at an optimal moisture content. Obviously, insufficient aeration of the soil with excess moisture aggravates the deleterious effect of high soil acidity on plants.

An increase in soil acidity improves the solubility of many poorly soluble soil-derived salts and hence their availability to plants.

It should be noted that the effect of acidity on nutrient uptake is largely determined by soil properties. For instance, a decrease in pH in soils containing large amounts of iron, aluminium, and manganese leads to higher mobility of these elements and their accumulation in plants to toxic concentrations, which adversely affects plant development and, consequently, uptake of other nutrients.

It is also known that Fe^{3+} and Al^{3+} ions form poorly soluble, hence unavailable, compounds with phosphorus, molybdenum, and some other nutrients.

The buffering capacity of the soil, that is, its ability to withstand changes in the medium pH, and the presence of calcium mitigate the negative effect of high soil acidity on plants.

It should be remembered that the effect of liming on the import of various nutrients into plants largely depends on their concentration and ratio.

Weakly acidic reaction of the medium (pH $\approx$ 6.5) is optimal for the growth and productivity of most farm crops.

Under natural conditions, soil reaction varies widely: from pH 2.5-3 in sphagnum peats to pH 9-10 in sodic soils.

Rin'kis studies indicate that decreasing acidity strongly inhibits the uptake of manganese, cobalt, and zinc and, to a much lesser degree, potassium and magnesium. The investigator ranged the examined nutrients in decreasing order of

their import rate, in the case of an acidified medium, as follows:

Mn, Co, Zn, Cu, P, Fe, B, Mg, K, N, Mo.

In reality, Mn and Zn are usually deficient in calcareous soils.

The pH value of the soil solution exerts a definite effect on the vital activity of soil microorganisms.

Plants are more tolerant to adverse reaction of the medium on soils characterized by more pronounced exchange and buffering capacities.

2.10 Physiological Reaction of Salts

The physiological reaction of salts is among the other factors determining the uptake of nutrients by plants from inorganic fertilizers.

According to their chemical properties, all salts used to fertilize plants may be hydrolytically acidic, hydrolytically alkaline, or neutral.

In the course of growth, plants selectively take up ions, and even if chemically neutral salts are introduced into the solution, their physiological reaction may be different.

The role of some or other cations and anions in plant nutrition determines the different rates of their uptake. As a result, all ions remaining in the nutrient solution are responsible for its acidity or alkalinity.

The physiological acidity of a fertilizer is basically its capacity to acidify the medium, associated with uptake of cations in preference to other salt components.

Similarly, the physiological alkalinity of a fertilizer is its capacity to alkalize the medium, associated with predominant uptake of anions.

Thus, when defining the effect of nutrient mixtures on variations in pH of the medium, one must take into consideration not only the chemical but also physiological reaction of the salts.

Although the physiological reaction of salts is more pronounced in water and sand cultures, that is, non-buffer media, it should be taken into consideration in practical applications at high fertilizer rates, especially in the case of low-buffer soils of arenaceous texture with a low humus content.

Application of physiologically acidic salts must be preceded by liming. As a rule, when salts containing nitrogen are used, it is precisely this element that is taken up by plants in the first place. Therefore, ammonium salts are physiologically acidic, while nitrates are physiologically alkaline.

For example, sodium nitrate dissociates into Na^+ and NO_3^-, the anion NO_3^- being taken up by plants in greater amounts than the cation Na^+; the hydrolytically alkaline salt $NaHCO_3$ appears in the solution in addition to $NaNO_3$. Salts KNO_3, $Mg(NO_3)_2$, and $Ca(NO_3)_2$ behave in a similar manner.

The nutrient solution undergoes intensive acidification as a result of the faster uptake of ammonium which forms in the dissociation of NH_4Cl and $(NH_4)_2SO_4$. Application of these salts calls for neutralization of the resulting acids by preliminary liming.

As a consequence of the rapid formation of ammonia from the dissociation of ammonium nitrate, this salt is physiologically acidic, as shown by Pryanishnikov's experiments.

The physiological reaction of ammonium nitrate is governed by a number of factors determining the uptake of nitrate and ammonium nitrogen by plants from this fertilizer. The physiological acidity of ammonium nitrate is usually much weaker than that of purely ammonium salts.

The physiological acidity of potassic salts is even weaker, as compared to ammonium salts. It has been established that, in cultivation of crops with low potassium requirements, such as oat and barley, potassic salts are physiologically almost neutral, while in the case of sugar beet, sunflower, and maize, taking up sizable amounts of potassium, these salts are physiologically acidic (potato, tobacco, and flax also take up a lot of potassium).

The stability of the nutrient solution pH depends on its composition. For example, if a solution contains much calcium bicarbonate $Ca(HCO_3)_2$, resulting from dissolution of $CaCO_3$ in carbonated water, the excess acid will react with it, yielding a calcium salt, water, and carbon dioxide:

$$Ca(HCO_3)_2 + H_2SO_4 = CaSO_4 + 2H_2O + 2CO_2$$

Such a solution exhibits buffer properties to a certain degree, and no perceptible changes in pH of the solution occur while

it still contains calcium bicarbonate. The buffer properties of soils are to a great extent dependent on their exchange capacity and composition of the exchangeable cations.

2.11 Effect of Soil Microorganisms on Inorganic Nutrient Uptake

Topsoil contains anywhere from 3 to 8 tons of bacteria per hectare.

Autotrophic bacteria fix the carbon of CO_2 by way of photosynthesis or using the chemical energy of oxidation of certain mineral substances, i.e. by chemosynthesis. Photosynthetic capacity is inherent in green and purple sulphur bacteria. Nitrifying, iron, and colourless bacteria belong to the chemosynthetic group.

Heterotrophic bacteria take up carbon from organic compounds.

The activity of soil microorganisms is a major factor of conversion of nutrients in the soil and their availability to plants. Under aerobic and anaerobic conditions, heterotrophic bacteria induce ammonification or, in other words, degradation of nitrogenous organic compounds to ammonia. Nitrifiers oxidize ammonium to nitrates. The process is promoted by a favourable water regime in adequately aerated soils. In the case of active nitrification, up to 200 kg of nitrates may be accumulated in a hectare of soil during the vegetation period.

Under conditions of poor soil aeration, the process of denitrification, that is, reduction of nitrates to molecular nitrogen or its intermediate compounds, is activated. In poorly aerated soils, denitrification may lead to substantial nitrogen losses.

The oxidation of hydrogen sulphide, elemental sulphur, and sulphur compounds to H_2SO_4 is termed sulphofication. This process is induced by sulphur, or thionic, bacteria. Sulphuric acid facilitates conversion of sparingly soluble mineral salts, particularly phosphates, into readily soluble ones and, combining with bases, yields sulphates taken up by plants.

The population and species composition of bacteria are strongly influenced by application of fertilizers.

In an experiment, for example, the population of bacteria had reached, by the end of summer, 350 million per gram without any fertilizers being applied, 610 million after manuring, 530 million after manuring and liming, and 540 million after application of manure plus phosphorus and potassium. The population of microorganisms depends on the type of soil, content of organic matter in it, and the state of its cultivation. One gram of soddy podsolic soil contains 600 to 1000 million microorganisms, their population in the same amount of cultivated soddy podsolic soil being 1000 to 2000 million, in chernozem, 2000 to 2500 million, and in cultivated chernozem, 2500 to 3000 million.

Induced by myriad microorganisms in the soil, ammonification and nitrification processes occur invariably under conditions of good aeration. As a result, the soil accumulates increasingly large amounts of nitrogen that can be taken up by plants, its mobility and availability being increased along with leachability from the topsoil. If soil aeration is poor, denitrification becomes predominant with the result that nitrogen is lost as a gas.

To minimize losses of fertilizer nitrogen, new formulations of nitrogen fertilizers are being constantly sought. Application of fertilizers is scheduled to comply with the periods of intensive nutrient uptake by plants, fertilizer preservatives, such as nitrification inhibitors, are extensively used, and so on.

The rate and orientation of microbiological soil processes govern the uptake of nutrients by plants. Living microorganisms mobilize the nutrients present in the soil in unavailable forms. Generally, microbiological processes are especially intensive in the rhizosphere of the root system. Consequently, the rhizosphere accumulates much greater amounts of available inorganic nutrients in spite of their being actively absorbed by the root system (Table 2.20).

The process of mobilization induced by microorganisms has most intensively been studied in relation to nitrogen. By far most of its reserves are contained in the soil as part of the organic compounds of humic origin and can be taken up by plants only after it has been digested by soil microorganisms.

The pronounced positive effect of the soil microflora is due to the capacity of some microorganisms to develop in

Table 2.20. Content of Available Inorganic Phosphorus and Potassium Nutrients in the Root Zone and in the Soil (mg per 100 g of dry soil)

Crop	P_2O_5		K_2O	
	around roots	rhizosphere	around roots	rhizosphere
Barley	18.6	22.5	9.3	12.8
Winter wheat	37.2	43.2	6.6	27.9
Oat	31.5	34.5	10.7	34.4
Clover	16.2	21.9	6.4	8.2

symbiosis with higher plants. A case in point is legumes capable of taking up atmospheric nitrogen and enriching the soil with it owing to their symbiosis with *Rhizobium*.

A major role in the nitrogen balance of soils, especially in a humid climate and in soils with abundant organic matter, is played by free-living nitrogen-fixing microorganisms.

Under certain conditions, the soil microflora around roots may exert not only a positive but also negative effect in view of the fact that some microorganisms consume a certain amount of inorganic compounds for their nutrition, therefore, the reserve of nutrients necessary for higher plants is somewhat depleted. The amount of such "biological fixation" is insignificant, though, and does not harm plants in any perceptible way. However, when the soil receives fertilizers with a high C : N ratio, such as straw manure, straw, and the like, microorganisms multiply frenetically, consuming sizable amounts of nitrogen, phosphorus, and other macro- and micronutrients. As a result, less nutrients are at plants' disposal. This is precisely what accounts for a decrease in crop yield within the first year after incorporation of straw into the soil.

The biological fixation of nutrients by microorganisms is usually of short duration. After dying away, microorganism cells become mineralized releasing nutrients. This normally happens during the second year after the soil has received fertilizers rich in carbon.

Increased fertilizer rates significantly affect the vital activities of soil microorganisms. As a rule, application of large amounts of nitrogen fertilizers activates the mobilization of

soil nitrogen by microorganisms and its uptake by plants. In particular, application of both inorganic fertilizers and especially manure gives a boost to propagation of nitrifiers and the nitrification process itself.

Humic acid preparations are decomposed by soil microflora much faster when nitrogen and organic fertilizers are added to them. The reason is that in a richer nutrient medium the number of microorganisms actively attacking humic com pounds rapidly increases. The positive effect of microorganisms is also manifest in that individual microbial metabolites in the soil stimulate seed germination and many vital processes in plants.

Anhydrous ammonia incorporated into the soil in small amounts (30 to 90 kg/ha) produces a stimulating effect on nitrification which is most intensive in a weakly alkaline medium. Higher rates of ammonia nitrogen and resulting higher alkalinity of the soil solution (pH 9.5-10) inhibit the activity of nitrifying bacteria.

Ammonia produces a toxic effect on other soil microorganisms as well. When ammonia is introduced at a rate of more than 120 kg/ha, the population of fungi, bacteria, and actinomyces is decreased temporarily. The toxic effect of ammonia is often confined to the zone extending to 6-8 cm from the application point and to a period of 5 to 10 days in the case of bacteria and 10 to 20 days in the case of fungi and actinomyces, after which their microbiological activity flares up.

As ammonia is being nitrified, the pH value gradually decreases (especially in light soils) to a level below the initial. Therefore, the increase in soil acidity as a result of application of ammonia fertilizers must be periodically ajusted by liming in order to maintain pH at a level most favourable for cultivation of major farm crops.

Intensification of agriculture calls for steadily increasing chemical control of weeds, crop diseases, and pests. Cultivation procedures also undergo changes: in some regions, conventional fallowing is replaced by the "chemical" one, that is, multiple application of herbicides. Weed control is conducive to accumulation of soil moisture. It should be borne in mind, however, that agricultural chemicals may adversely affect the soil microflora and a great deal of caution and moderation should be exercised when using pesticides.

2.12 Response of Plants to Nutrition Conditions at Different Stages of the Vegetation Period. Periodicity of Plant Nutrition

Different stages of the plant vegetation period are characterized by biochemical processes following various pathways at different rates. The uptake of nutrients throughout the vegetation period is irregular. A rational fertilizer system must provide, with due account for the plant requirements varying throughout the life cycle, for adequate supply of nutrients in appropriate amounts, ratios, and forms.

Inadequate supply of nutrients at a particular stage of development may reduce crop yields and lower the crop quality.

It is especially important to supply sufficient amounts of nutrients to plants during the so-called critical period when the uptake rate may be limited but nutrient deficiency strongly inhibits plant growth and development, just as during the period of maximal uptake, which is characterized by the highest nutrient import rates.

High sensitivity to both deficiency and excess of inorganic nutrients is observed in plants during the initial stage of their growth, which is critical insofar as phosphorus nutrition is concerned (Table 2.21).

Table 2.21. Effect of Periodic Phosphorus Uptake on Barley Yields

Nutrition conditions	Percentage yield	
	total	grain
Normal phosphorus uptake throughout the vegetation period	100	100
No phosphorus uptake during the first 15 days	17.4	0
No phosphorus from the 45th through the 60th day	102	104

The increased requirements of young plants for inorganic nutrition can be explained by the high intensity of the synthetic processes occurring over this period in plant organisms

while the root system is weak. For example, in grain cereals, initiation and differentiation of the reproductive organs start as early as during expansion of the first three or four leaves. Nitrogen dificiency during this period results in formation of fewer spikelets and lower yields. A subsequent increase in nitrogen to the normal level cannot remedy the damage sustained by the plant within this space of time (Table 2.22).

Table 2.22. Nitrogen Nutrition and Barley Yields (g per vessel)

Nutrition conditions	Straw	Grain
Nitrogen available throughout the vegetation period	26.1	6.4
No nitrogen during the first 15 days	4.5	0
Same, from the 15th through the 30th day	19.4	4.2
Same, from the 30th through the 40th day	29.1	8.7
Same, from the 45th through the 60th day	29.4	7.7
Same, after heading	18.6	3.8

The nutrient uptake rate at different developmental stages spans a wide range in different plants. For example, in one of the experiments, sugar beet plants took up 2 kg of nitrogen, phosphorus, and potassium, each, during the first month, then, during the second month, 96 kg of N, 34 kg of P_2O_5, and 133 kg of K_2O per hectare.

Grasses and sugar beet are characterized by prolonged uptake of nutrients. Hemp, on the other hand, is known for a short period of intensive nutrient uptake, taking up 75 per cent of the total nutrient requirement within the period from budding to flowering.

The maximum amount of inorganic nutrients is taken up by spring grain crops in the period from the shooting to heading stage. For instance, wheat was found to take up about 76 per cent of the maximum requirement for nitrogen, phosphorus, and potassium at the heading stage, barley, about 67 per cent, and oat, 47 per cent (Table 2.23).

Cabbage takes up the maximum amount of nutrients during head formation (Table 2.24).

Table 2.23. Nutrient Uptake by Spring Grain Crops (% of the maximum requirement)

Growth stage	Wheat			Barley			Oat		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O	N	P_2O_5	K_2O
Heading	71	68	88	71	56	73	51	36	54
Flowering	97	100	100	96	74	100	82	71	100
Complete ripeness	90	93	67	100	100	64	100	100	83

Table 2.24. The Dynamics of Nutrient Uptake by Cabbage (% of the maximum requirement)

Growth stage	From the onset of vegetation		
	N	P_2O_5	K_2O
Planting (June 10)	0.17	0.14	0.12
Head formation (July 27)	30.50	21.80	24.20
Loose head (September 7)	96.40	100.00	96.60
Table ripeness	100.00	90.50	100.00

The uptake of nutrients by plants is characterized by different rates. For example, cotton takes up nitrogen at a higher rate at the beginning of growth, while at the flowering and ripening stages it takes up more phosphorus and potassium (Table 2.25).

Table 2.25. Nutrient Uptake by Cotton (% of the total uptake throughout the vegetation period)

Vegetation period	N	P_2O_5	K_2O
From the beginning of growth to budding	3-5	3-5	2-3
From budding to flowering	25-30	15-20	15-20
From flowering to ripening	65-70	75-80	75-80

Cereals are usually more demanding insofar as nitrogen nutrition is concerned during formation of the assimilating system and differentiation of the reproductive organs. Sugar beet requires more potassium during sugar accumulation.

Table 2.26. Effect of Nitrogen Deficiency on Flax Yield at Different Development Stages

Nutrition conditions	Plant weight (%)
Adequate nitrogen supply throughout the vegetation period	100.0
No nitrogen from branching to budding	38.3
No nitrogen from budding to harvesting	99.0

Flax is more sensitive to the nitrogen nutrition level in the period from branching to budding (Table 2.26) and to that of potassium nutrition in the period from budding to flowering (Table 2.27).

Table 2.27. Effect of Potassium Deficiency on Flax Yield at Different Development Stages

Nutrition conditions	Number of bolls
Adequate potassium supply throughout the vegetation period	42
No potassium during the first 22 days	43
No potassium from budding to harvesting	9

Cucumber plants need more nitrogen for the formation of the assimilating system and more phosphorus prior to flowering. At the fruit bearing stage, cucumber plants require greater amounts of nitrogen and potassium.

Thus, at the initial stage of growth, plants require more phosphorus as opposed to nitrogen and potassium. Intensification of nitrogen and partially phosphorus nutrition at the budding and flowering stages leads to higher cereal crops. The increased nitrogen nutrition during leafing and the sub-

sequent intensification of phosphorus and potassium uptake ensure high yields of root and tuber crops.

The nitrogen requirement of most plants decreases by the beginning of fruit formation, phosphorus and potassium becoming predominant in plant nutrition. However, during the fruit-bearing period as a whole, the nutrient uptake rate goes down and, by the end of the vegetation period, the vital activity of plants is sustained primarily through re-utilization of the accumulated nutrients.

In developing a fertilizer system, one must take into account that plants require equal amounts of nutrients throughout the vegetation period. Notably, the main fertilizer must provide for plant nutrition throughout the vegetation period, which is why all organic and almost all inorganic fertilizers to be used are usually applied before seeding.

To supply plants with nutrients, particularly phosphorus, fertilizers are initially applied at seeding (drilling and hole application).

The yield of a crop and its quality can be controlled by dressing at different stages of the vegetation period. Dressing may improve the uptake of a particular nutrient by plants during the most critical periods or as soon as a nutrient is found to be deficient.

The uptake rate, or nutrient requirement, constantly changes not only throughout the vegetation period, but also at different hours of a day. Virtually all vital processes have been found to obey daily periodicity.

Appropriate conditions for meeting the nutrient requirements of plants can best be created when they are grown on artificial nutrient media. The cultivation of plants under controlled conditions without soil has been steadily gaining in importance.

Significant advances in the basic theory of plant nutrition and cultivation under artificial conditions must be credited to Pryanishnikov and his school.

Of particular importance for growing plants on artificial media are the composition and concentration of the nutrient solution, as well as the way in which it is used over the vegetation period. The conditions of nutrition must change with the age of plants. By temporarily stopping the influx of nutrients at certain stages of the vegetation period it is

possible to intensify development of the root system. Substitution of water for the nutrient solution may cause plants to starve temporarily, thereby stimulating the process of tuber formation in potatoes and fruit setting in tomatoes, i.e. inducing early maturity.

Of particular interest is the manifestation of daily periodicity in nutrient uptake. It occurs under both variable and invariable environmental conditions and takes the form of an endogenous rhythm. The daily periodicity determined by the biological characteristics of plants allows them to actively adapt themselves to the constantly changing environmental conditions. The endogenous daily or circadian rhythms gradually recede under invariable conditions and are restored again as soon as the latter are changed. The capacity of plants to vary their circadian period improves their chances for survival.

Annual, seasonal, and daily rhythms are distinguished; in addition, plants undergo rhythms pulsating at periods ranging from several hours to a few seconds. Pulsating rhythms with short active periods have been discovered in the absorbing and secreting activities of roots and other physiological processes in plants.

There is a growing tendency to cultivate vegetables and other farm crops in hothouses.

Cultivation under controlled conditions permits raising the yields of most crops. It is noteworthy here that the productivity of crops can be increased by periodic nutrition.

The periodic nutrition approach is especially promising for hydroponics where it can substantially enhance plant productivity without spending more money on fertilizers.

Chapter 3

Soil Properties in the Context of Plant Nutrition and Application of Fertilizers

The total amount of nutrients in the soil and the content of their available forms as well as the rate of nutrient transformation from the unavailable to available state and vice versa are the major factors determining the nutrition conditions of plants and their requirements for fertilizers.

When the soil contains large amounts of available nutrients, plants need less fertilizers, and vice versa. The total amount of available nutrients in various soils depends on their composition and properties, therefore, the response of plants to fertilizers and their effectiveness in different soils are also different.

Once applied, fertilizers undergo diverse transformations in the soil with the result that the solubility of the nutrients they contain changes along with their mobility in the soil and availability to plants. The exact transformations of fertilizers in the soil and their rate depend on soil properties. At the same time, fertilizers themselves exert a considerable influence on the soil: they enrich it with nutrients, alter the pH value of the soil solution, rate and course of microbiological processes, and other properties determining soil fertility. This is why knowledge of soil composition, properties, and the physicochemical, chemical, and biological processes taking place in the soil is instrumental for understanding the transformations of fertilizers in it, their activity in different soils, and hence, their effective use with due account for the cultivated crops as well as soil and climatic conditions.

3.1 Soil Composition

The soil is constituted by a solid phase, a liquid phase or soil solution, and a gas phase or soil air, all these phases interacting most intimately.

Soil air differs from the atmospheric one by a higher content of carbon dioxide and a lower content of oxygen. In the soil, oxygen is constantly taken in and CO_2 released during decomposition of the organic matter by microorganisms, respiration of plant roots, and as a result of some chemical reactions. Atmospheric air contains 0.03 per cent of carbon dioxide, while its content in soil air ranges from 0.3 to 1 per cent (sometimes even to 2, 3, and more per cent).

The CO_2 content in soil air depends on the rate of the gas exchange between the soil and the atmosphere. The carbon dioxide forming in the soil is partially released into the atmosphere, the rest being dissolved in soil moisture. Diffusion of carbon dioxide from the soil enriches the surface air that envelops the leaves of plants. Under normal aeration conditions, one cubic metre of the soil beneath plants releases anywhere from two to ten litres of CO_2 per day in summer, taking in the same amount of O_2. The increased CO_2 content in the surface air layer provides better conditions for uptake of this gas by plants and is conducive to higher yields. Carbon dioxide dissolves in soil moisture to yield carbonic acid which dissociates into H^+ and HCO_3^- ions and acidifies the soil solution:

$$CO_2 + H_2O \quad H_2CO_3 \rightarrow H^+ + HCO_3^-$$

Enrichment of the soil solution with carbon dioxide enhances its capacity to dissolve inorganic soil nutrients (calcium phosphates and carbonates, etc.), promoting their conversion into available forms. At the same time, an extremely high carbon dioxide content and oxygen deficiency in soil air (e.g. in the case of excess moisture content and poor soil aeration) adversely affect the development of plants and microorganisms. Oxygen deficiency inhibits the respiration and growth of roots and reduces nutrient uptake by plants. If soil aeration is poor, anaerobic reduction processes become predominant in the soil as soon as the oxygen content in soil air drops. Good aeration creates more favourable conditions for the development of soil microorganisms, nutrition, and growth of plants.

Soil solution is the most mobile and active part of the soil, in which various chemical processes occur and from which plants take up nutrients (salts) directly. Depending on the

soil type and other factors, the soil solution contains anions (HCO_3^-, OH^-, Cl^-, NO_3^-, $H_2PO_4^-$, etc.), cations (H^+, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, etc.), and water-soluble organic substances and dissolved gases (oxygen, carbon dioxide, ammonia, etc.). It receives salts as a result of weathering and breakdown of minerals, decomposition of organic substances in the soil by microorganisms, and application of organic and inorganic fertilizers. As far as plant nutrition is concerned, it is especially important that the soil solution contain K^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, SO_4^{2-}, and $H_2PO_4^-$ with their continuous replenishment.

The total amount of salts in the soil solution varies from hundredths of a per cent (in soddy podsolic soils) to several per cent (in saline soils). The content of water-soluble salts in soils is usually in the neighbourhood of 0.05 per cent. Their excess in the soil (above 0.2%) produces a harmful effect on plants.

The composition and concentration of the soil solution may vary perceptibly under the effect of a number of factors. Its salt content increases when fertilizers are applied, the soil moisture content is reduced, and mineralization of the organic matter is intensified. The uptake of nutrients by plants, leaching of soluble compounds into the underlying horizons or their transition to insoluble forms bring down the soil solution concentration. The composition and concentration of salts in the solution also depend on its interaction with the solid phase of the soil and on the exchange reactions between the solution and soil colloids.

The **solid phase of the soil*** contains the bulk of nutrients for plants. It consists of the mineral, or inorganic, portion accounting for 90 to 99 per cent of the solid phase in most soils and the organic portion which is a major factor of their fertility. The average chemical (elementary) composition of the solid phase (in %) is as follows (according to Vinogradov):

* It would be more correct to speak of a "combination of solid phases" in view of the heterogeneity of the soil. However, the term "solid phase" is used for simplicity, implying the entire combination.

Oxygen	49.0	Barium	0.05	Gallium	(10^{-3})
Silicon	33.0	Strontium	0.03	Tin	(10^{-3})
Aluminium	7.1	Zirconium	0.03	Cobalt	8×10^{-4}
Iron	3.7	Fluorine	0.02	Thorium	6×10^{-4}
Carbon	2.0	Chromium	0.02	Arsenic	5×10^{-4}
Calcium	1.3	Chlorine	0.01	Iodine	5×10^{-4}
Potassium	1.3	Vanadium	0.01	Cesium	5×10^{-4}
Sodium	0.6	Rubidium	6×10^{-3}	Molybdenum	3×10^{-4}
Magnesium	0.6	Zinc	5×10^{-3}	Uranium	1×10^{-4}
Hydrogen	(0.50)	Cerium	5×10^{-3}	Beryllium	(10^{-4})
Titanium	0.46	Nickel	4×10^{-3}	Germanium	(10^{-4})
Nitrogen	0.10	Lithium	3×10^{-3}	Cadmium	5×10^{-5}
Phosphorus	0.08	Copper	2×10^{-3}	Selenium	1×10^{-6}
Sulphur	0.08	Boron	1×10^{-3}	Mercury	(10^{-6})
Manganese	0.08	Lead	1×10^{-3}	Radium	8×10^{-11}

Oxygen accounts for almost half of the solid phase, silicon, for a third, aluminium and iron, for more than 10 per cent, the rest of the elements accounting for only 7 per cent.

All of the above elements are present in the inorganic portion of the soil, forming part of various inorganic compounds. Carbon, hydrogen, oxygen, phosphorus, and sulphur can be found in both inorganic and organic portions. Almost all of nitrogen occupies the organic portion.

3.2 Inorganic Portion of the Soil

The inorganic portion of the soil is made up primarily of particles of various minerals ranging in size from millionths of a millimetre to one and more millimetres. Soil minerals are divided into primary and secondary. The *primary minerals* include quartz, feldspars, micas, hornblendes, and pyroxenes. They are present in soils mainly in the form of sand (from 0.05 to 1 mm in size) and silt (from 0.001 to 0.05 mm) particles and, to a lesser extent, in the form of clay (less than 0.001 mm) and colloidal (less than 0.25 μm) particles. When primary minerals are broken down by chemical processes (hydration, hydrolysis, and oxidation) and the activity of some organisms, hydrates of sesquioxides, silica hydrates, various salts, and *secondary minerals*, also known as clay minerals (kaolinite, montmorillonite, hydromicas, etc.) form in the soil. They are present in the soil mostly as clay and colloidal particles and, less often, as silt particles.

According to their chemical composition, minerals are

divided into silicon oxides, or silicates, and aluminium silicates, or alumosilicates.

The most common *silicon oxide* is quartz (SiO_2) which is present predominantly in the form of sand and silt particles. Almost in all soils its content exceeds 60 per cent, reaching and even exceeding 90 per cent in sandy soils. Quartz is a highly stable and hard mineral, chemically inert to a high degree, and normally taking no part in the chemical reactions occurring in the soil.

Aluminium silicates (alumosilicates) are represented in the soil by various primary and secondary minerals. The most common of the primary alumosilicates are feldspars which are subdivided into potash feldspars (orthoclases $KAlSi_3O_8$) and soda-lime ones (plagioclases) consisting of isomorphic mixtures of anorthite, $CaAl_2Si_2O_8$, and albite, $NaAlSi_3O_8$, in different ratios. Next come micas, including, in decreasing order of occurrence, potash mica, or muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$, iron-magnesium mica, or biotite, $K(Mg, Fe)_3(AlSi_3O_{10})_5(OH, F)_2$, and magnesium mica, or phlogopite, $KMg_3(AlSi_3O_{10})(OH, F)_2$. Hornblendes and pyroxenes occur sporadically in soils. As they gradually break down, feldspars and mica become sources of potassium, calcium, magnesium, iron, and other nutrients for plants.

The secondary alumosilicate minerals contain primarily silicon, aluminium, oxygen and hydrogen, as well as small amounts of calcium, magnesium, potassium, and iron.

According to some of their properties (lattice structure, degree of dispersion, etc.), the secondary minerals include the montmorillonite, kaolinite, and hydromica groups.

The montmorillonite group includes montmorillonite, $Al_2Si_4O_{10}(OH)_2 \cdot nH_2O$, beidellite $Al_3Si_3O_9(OH)_3 \cdot nH_2O$, and some other minerals. Montmorillonite clays are characterized by a high degree of dispersion, swelling capacity, stickiness, and viscosity.

The kaolinite group of minerals is represented by kaolinite, $Al_2Si_2O_5(OH)_4$, and halloysite, $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$. Kaolinite clays are less dispersed than the montmorillonite ones, swell to a lesser extent, and are not as viscous. Gorbunov's studies have shown that in soddy podsolic and chernozemic soils formed on loamy substrates micas and montmorillonite prevail among the highly dispersed

minerals, while kaolinite is present as a minor component or does not occur at all. Sizable amounts of kaolinite can be found only in red and yellow soils as well as soddy podsolic soils formed on granite.

Hydromicas form from feldspars and micas. The most common ones include hydromuscovite (illite), $KAl_2[(SiAl)_4O_{10}](OH)_2 \cdot nH_2O$, hydrobiotite, $K(MgFe)_3[(AlSi)_4O_{10}](OH)_2 \cdot nH_2O$, and vermiculite, $(MgFe^{2+}, Fe^{3+})_2[(Al, Si)_4O_{10}](OH)_2 \cdot 4H_2O$.

The secondary alumosilicate minerals differ in lattice structure, degree of dispersion, and other parameters but, on the other hand, they share some common properties. They are present in the soil as crystals varying in size from a few microns to tenths and hundredths of a micron. By virtue of their high dispersion, these minerals have an extended surface and exhibit a high absorbing capacity.

Along with the crystalline silicate and alumosilicate minerals, the inorganic portion of the soil also contains amorphous substances. Predominant among the latter are aluminium ($Al_2O_3 \cdot nH_2O$), ferric ($Fe_2O_3 \cdot nH_2O$), and silicon ($SiO_2 \cdot nH_2O$) hydroxides, these substances precipitating in the soil in the form of amorphous colloids (gels). Gradually losing water, they may be crystallized, whereby silicon hydroxide converts into secondary quartz, while aluminium hydroxide and ferric hydrate form gibbsite, $Al_2O_3 \cdot 3H_2O$, boehmite, $Al_2O_3 \cdot H_2O$, goethite, $Fe_2O_3 \cdot H_2O$, limonite, $2Fe_2O_3 \cdot 3H_2O$, and other minerals. They are present in large amounts in red, yellow, and some soddy podsolic soils.

The soil also contains various salts: carbonates, sulphates, nitrates, chlorides, and phosphates of calcium, magnesium, potassium, and sodium. Most of these salts (e.g., potassium and sodium nitrates, chlorides, carbonates, and phosphates) are readily soluble in water and, therefore, are present in soils in small amounts. Such less readily soluble salts as calcium carbonate, magnesium carbonate, and calcium sulphate account for a significant portion of the solid phase in some soils. All soils always contain poorly soluble salts of phosphoric acid (calcium, magnesium, iron, and aluminium phosphates). The various fractions of the inorganic portion of the soil differ in particle size as well as in the mineralogical and chemical composition.

The predominant minerals in sand and coarse silt are quartz and feldspars. In smaller fractions (medium and fine silt), the content of these minerals diminishes, while that of micas and hornblendes increases. The fine (< 0.001 mm) clay or colloidal fraction consists primarily of secondary aluminosilicates. Because of their different mineralogical composition, some fractions also differ in chemical composition and in the content of the most common soil nutrients (Table 3.1).

Table 3.1. Approximate Chemical Composition of Different Soil Fractions

Fraction, mm	Content (weight, %)						
	Si	Al	Fe	Ca	Mg	K	P
1.0-0.2	43.4	0.8	0.8	0.3	0.3	0.7	0.02
0.2-0.04	43.8	1.1	0.8	0.4	0.1	1.2	0.04
0.04-0.01	41.6	2.7	1.0	0.6	0.2	1.9	0.09
0.01-0.002	34.6	7.0	3.6	1.1	0.2	3.5	0.04
>0.002	24.8	11.6	9.2	1.1	0.6	4.1	0.18

Larger soil particles (sand and silt) contain more silicon but less aluminium and iron. The smaller the particle size, the lower the silicon content and the higher that of aluminium, iron, potassium, calcium, magnesium, and phosphorus.

Humus (and the constituent nitrogen) is also localized in the finer soil fraction. Hence, the clay and colloidal fractions are more important as sources of nutrients for plants. Besides, these fractions are more active and govern the adsorption processes in the soil and its absorbing capacity.

Since individual soil fractions differ in the minerals they contain, the mineralogical and chemical composition of soils of different texture is dissimilar. Sandy and sandy loam soils consist of quartz and feldspars, loamy soils comprise a mixture of primary and secondary minerals, and argillaceous, or clayey, soils consist predominantly of secondary clay minerals with a small amount of quartz.

The texture of soil determines many of its physical, physicochemical, and chemical properties. The content of iron,

calcium, magnesium, potassium, and other nutrients that are present only in the inorganic portion of the soil, as well as that of phosphorus present in both inorganic and organic portions, is determined mainly by their texture. Heavier argillaceous and loamy soils are richer in these nutrients than sandy and sandy loam soils.

3.3 Organic Matter of the Soil

Organic matter is by far the most important soil component. The content of organic matter, including humus, in the arable layer of different soils varies widely (Table 3.2).

Table 3.2. Humus Content in Main Soil-Types (according to Tyurin)

Soils	Humus content in the arable layer (%)	Humus reserves (t/ha) in the soil layer to a depth	
		of 20 cm (on the average)	of 100 or 120 cm
Soddy podsolic	2-4	53	80-120
Grey forest podsolized	4-6	109	150-300
Chernozem:			
leached	7-8	192	500-600
deep	10-12	224	650-800
ordinary	6-8	137	400-500
sourthern	4-5		300-350
Dark chestnut	3-4	99	200-250
Chestnut and light chestnut	1.5-4	—	100-200
Sierozem	1-2	37	50
Red (krasnozem)	5-7	153	150-300

The organic portion of the soil represents a complex combination of various organic substances that can be divided into the following two groups:

(1) nonhumified organic substances of plant or animal origin;

(2) organic substances of a specific nature: humus or mull.

The group of nonhumified organic substances includes essentially dead plant residues, not yet decomposed or half-decomposed, and remains of soil animals (worms, insects, etc.) or microorganisms.

According to Tyurin, cultivated soils receive each year five to eight tons of plant residues per hectare, which account for 7 to 8 per cent of the total organic matter in the arable layer of soddy podsolic soils and 1 to 2 per cent, in that of chernozems. The weight of bacteria (in a soil layer 20 cm deep) ranges from 0.7 to 2.7 tons (5-8 tons according to some sources) per hectare, which corresponds to a maximum of 1 to 2 per cent of the total organic matter. The soil also contains very small amounts of various, chemically individual organic compounds that are intermediate products of decomposition of plant residues, microorganisms, and soil animals: namely, carbohydrates (cellulose, hemicellulose, starch, etc.), organic acids, proteinaceous and other nitrogenous substances (amino acids, amides, etc.), fats, resins, aldehydes, polyuronic acids and their derivatives, polyphenols, tanning agents, lignin, and so on. As a whole, the nonhumified substances account for about 10 to 15 per cent of the total organic matter in the soil. Yet they play a major role in soil life and fertility. Some of them, organic acids for example, are involved in the decomposition of soil minerals, others produce a stimulating or inhibitory effect on plant growth and development.

The nonhumified organic substances are a major source of nutrients for plants and decompose in the soil with relative ease. The nutrients they contain, such as nitrogen, phosphorus, sulphur and others, convert into the inorganic form available to plants. However, not all of the organic substances present in plant and animal residues are completely mineralized. As some of them decompose in the soil, they undergo conversion into organic substances of a specific nature and serve as sources of humic substances, i.e. high-molecular nitrogenous compounds. These account for 85 to 90 per cent of the total organic matter in the soil.

The humic substances are classified in the following categories differing in composition and properties: humic acids, fulvic acids (the latter used to be termed crenic and apocrenic acids), and humins.

The most extensively studied category at present is that of humic acids, including substances with similar composition and properties, but not quite identical. The elementary composition of humic acids from different soils is as follows:

52-62% C, 31-39% O, 2.8-6.6% H, and 3.3-5.1% N.

The molecular structure of humic acids is yet to be elucidated. Humic acids are currently considered to be complex high-molecular compounds of aromatic nature.

Humic acid molecules include aromatic, nitrogen-free and nitrogenous heterocyclic six- and five-membered rings bridged by —N—, —NH—, $-CH_2-$, and other groups.

Humic acids also contain carbohydrate residues (hexoses, pentoses, etc.) and organic nitrogenous compounds (peptides, amino acids, etc.) which seem to be associated with their aromatic nucleus via peripheral side chains. Other components of humic acid molecules include functional groups, such as three to six phenolic hydroxyls (—OH), three to four carboxyls (—COOH), methoxyls ($-O-CH_3$), and carbonyls (=C=O), determining the properties of humic acids and their interaction with the soil. The carboxy groups in humic acids are responsible for their acidic properties and involvement in the processes of exchange adsorption of cations.

The hydrogen of the carboxy groups may be replaced by various cations to yield salts known as humates, for example:

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2$$
$$2RCOOH + CaCO_3 \longrightarrow (RCOO)_2Ca + H_2O + CO_2$$

The humates of univalent cations (Na^+, K^+, NH_4^+) are water-soluble compounds. The predominant cation in most soils is calcium; therefore, forming in the first place are calcium humates, which are insoluble in water and precipitate in the soil in the form of colloids. The humates of magnesium and trivalent cations (Fe^{3+} and Al^{3+}) are also insoluble in water.

A permanent component of humic acids is nitrogen present in amounts varying from 3.5 to 5 per cent. Acid hydrolysis (6 *N* HCl) of humic acids causes about half the nitrogen to pass into solution, the hydrolysate containing amides, mono- and diamino acids in ratios typical of plant and animal proteins (Table 3.3). However, the hydrolyzable part of the humic acid nitrogen is represented not by proteins, but by products of their degradation, peptides and amino acids, present in the form of a weak link with the aromatic nucleus.

Table 3.3. Percentage Fractions of Nitrogenous Compounds in Humic Acid (according to A. A. Shmuk)

Fractions	of humic acid	of total humic acid nitrogen	of soluble humic acid nitrogen
Total nitrogen	3.20	—	—
Nitrogen passed into solution during hydrolysis	1.42	44.4	—
including: N of amides	0.36	11.2	25.4
N of monoamino acids	0.92	28.8	64.8
N of diamino acids	0.14	4.4	9.8
Nitrogen of the nonhydrolyzable residue	1.78	55.6	—

Hence, nitrogen is bound in the humic acid molecule in the form of peripheral chains and in the heterocyclic form. The non-hydrolyzable nitrogen in humic acids (accounting for 40 to 50 per cent of its total amount) seems to be represented by the nitrogen bound in the molecular nucleus in the heterocyclic form. This nitrogen portion is most stable to microbiological decomposition. The humic acid nitrogen constitutes anywhere from 15 to 30 per cent of the total nitrogen in various soils.

The next category of humic substances, fulvic acids, is represented essentially by high-molecular hydroxycarboxylic acids containing nitrogen. They differ from humic acids by a lighter colour, solubility in water and mineral acids, and a more pronounced capacity for acid hydrolysis.

The elementary composition of fulvic acids (according to Ponomareva) is as follows: 45-48% C, 5-6% H, 43-48% O, and 1.5-3% N. As compared to humic acids, fulvic ones are characterized by predominance of linearly polymerized carbon in the structure of their side chains and a smaller number of aromatic carbon networks. Just as humic acids, they contain phenolic hydroxyls, methoxyls, and carboxyls and are capable of exchange adsorption of cations. The calcium and magnesium salts of fulvic acids (fulvates) are water-soluble, their complex compounds with aluminium and iron are also characterized by high mobility and precipitate only within a narrow pH range. Fulvic acids are more mobile, and the

nitrogenous compounds in their molecules are bound less firmly and are more prone to acid hydrolysis than their counterparts in humic acids. The nitrogen of fulvic acids accounts for 20 to 40 per cent of the total soil nitrogen.

The humins of soil humus (humic substances insoluble in alkalis) are similar in nature to humic acids but are more intimately associated with the inorganic portion of the soil. This accounts for their higher resistance to acids and alkalis. The nitrogen of this humus fraction constitutes 20 to 30 per cent of the total soil nitrogen, is more strongly fixed, and better withstands decomposition by microorganisms.

Various types of soil differ not only in total, humus content but also in its composition, that is, ratio between humic and fulvic acids and their properties. The humus of soddy podsolic soils contains more fulvic acids and less humic ones than that of chernozems. The ratio of the latter to the former acids is 0.4 to 0.6 in soddy podsolic soils and 1 to 1.5 and even higher in chernozems. Unlike the humic acids of chernozems, the structure of those in soddy podsolic soils contains more side chains and much less cyclically polymerized carbon. This is why they are characterized by a broader range of particle sizes and a looser aggregation, which brings them closer to fulvic acids. These differences are largely responsible for the greater mobility of the organic matter, hence nitrogen, in soddy podsolic soils as opposed to chernozems.

Only an insignificant part of humic substances in soils are in the free state. Humic and fulvic acids enter into chemical and colloidochemical reactions with the inorganic portion of the soil to yield various organomineral compounds (humates of Ca, Mg, and Na, humates and mixed gels with aluminium and iron hydroxides or organomineral complexes with aluminium, iron, phosphorus, and silicon). Moreover, they are capable of being permanently adsorbed by argillaceous minerals, whereby they become less accessible to microorganisms. The interaction of humic substances with the inorganic portion of the soil and emergence of various forms of organomineral compounds play an important role in the fixation of humus in the soil.

Humic substances are relatively resistant (although to different degrees in various soils) to microbiological decompo-

sition and do not lend themselves as readily to mineralization as the organic compounds which form part of the plant residues received by the soil. However, no matter how slow, decomposition of humus in the soil is a continuous process. Perennial experiments indicate that long-continued cultivation of farm crops without fertilizing leads to a drastic depletion of the total humus and nitrogen reserves in the soil. In humus- and nitrogen poor soils, the content of these substances decreases over 30 to 50 years by 25 and even as much as 50 per cent of the initial level.

According to the results of perennial experiments, an average of 6 to 7 centners of organic matter per hectare are mineralized each year in the arable layer of soddy podsolic soils, the same figure for chernozems being in the neighbourhood of ten, which corresponds, respectively, to about 1 and 0.4-0.5 per cent. Accordingly, 30-35 and 50 kg of inorganic nitrogenous substances available to plants are formed per hectare. Since the content of nitrogen in the humus is about five per cent, twenty parts of humus must be mineralized per part of this element taken up by plants from the soil.

The decomposition of humus is particularly intensive in clean fallow where 60 to 120 kg of nitrate nitrogen may accumulate per hectare. One or two tons of organic matter must be mineralized to produce such an amount of nitrogen. Humus is continuously generated in the soil as plant residues keep being supplied into the soil and it undergoes disintegration and mineralization. Depending on which of these processes is predominant, the total humus content in the soil will either decrease or increase. Systematic application of organic and inorganic fertilizers not only increases crop yields, but also enables the humus and nitrogen reserves in the soil to be maintained at the same or even a higher level. The yield increase due to fertilizers is accompanied by greater amounts of afterharvesting residues being incorporated into the soil, whereby the content of the newly formed humic substances increases.

In spite of the relatively low content of organic matter in the soil, it is an important factor of soil fertility and plant nutrition.

Humic, fulvic, and other organic acids as well as the carbonic acid that form in the decomposition of organic sub-

stances induce gradual disintegration of silicate and alumosilicate minerals, dissolution of calcium and magnesium carbonates, phosphates, and other sparingly soluble salts. As a consequence, the nutrients they contain, such as calcium, magnesium, potassium, and phosphorus, are converted into an available form.

Organic matter is a major source of nutrients for plants. It contains almost all of soil nitrogen, a sizable portion of phosphorus and sulphur, and small amounts of potassium, calcium, magnesium, and other nutrients.

The bulk of soil nitrogen (up to 90 per cent) forms part of various humic substances, the remaining minor amount being found in non-humified organic compounds (proteins, amino acids, etc.) constituting plant residues and remains of animals and microorganisms. Organic phosphorus compounds account for 30 to 40 per cent, and even more, of the total content of these elements in the soil, the content of organic sulphur compounds reaching 90 per cent. As a result of decomposition of organic matter by microorganisms, nitrogen, phosphorus, sulphur, and other nutrients present in it pass into readily available inorganic compounds.

Organic substances affect plants directly. Some of them, for example benzoic acid and vanillin, are toxic even in tiny amounts. At the same time, most organic substances, such as humic acids in a highly dispersed state, individual compounds of the aromatic series, organic acids (acetic, propionic, succinic, and others), as well as the enzymes, antibiotics, growth substances, and vitamins present in the soil, sometimes stimulate the growth of plants cultivated in water and sand, when taken up in trace amounts.

Organic substances are the main source of nutrients and energy for most soil microorganisms. The activity of the latter is strongly influenced by the content of organic substances in the soil.

Organic substances are involved in adsorption processes (the higher their content in the soil, the more pronounced its absorbing and buffering capacities), improving soil structure, its moisture capacity, water and air permeability, and thermal regime.

3.4 Content of Nutrients and Their Availability in Various Soils

Various soils differ in composition of the inorganic portion, content and composition of the organic matter. Therefore, the content of basic nutrients in various soils differs too. The overall content of nitrogen, phosphorus, and potassium in the arable layer of various soils is as tabulated below. (See Table 3.4.)

Table 3.4. Overall Content of Nutrients in Various Soils

Soil	N		P_2O_5		K_2O	
	%	t/ha	%	t/ha	%	t/ha
Soddy podsolic sandy	0.02-0.05	0.6-1.5	0.03-0.06	0.9-1.8	0.5-0.7	15-21
Soddy podsolic loamy	0.05-0.13	1.5-4.0	0.04-0.12	1.2-3.6	1.5-2.5	45-75
Chernozem	0.2-0.5	6.0-15.0	0.1-0.3	3.0-9.0	2.0-2.5	60-75
Sierozem	0.05-0.15	1.5-4.5	0.08-0.2	2.4-6.0	2.5-3.0	75-90

The total content of nitrogen in soils is in direct proportion to the amount of humus; there is also more phosphorus in soils if they are rich in organic matter, while the potassium content is determined primarily by the texture of the inorganic portion of the soil.

In most soils, the overall content of nitrogen, phosphorus, and potassium is rather high, tens and hundreds of times exceeding the amount of these nutrients removed by a crop. However, the major part of nutrients is present in the soil in the form of compounds completely or almost unavailable to plants. Nitrogen is present mainly in the form of complex organic compounds (humic substances, proteins, etc.), most of phosphorus forms part of difficultly soluble inorganic compounds and organic substances, and most of potassium is found in insoluble alumosilicates.

The overall content of nutrients in the soil merely characterizes its potential fertility. To evaluate the effective fertility, that is, the actual capacity of the soil no ensure high

yields of farm crops, it is extremely important to take into account the content of available nutrients. Plants can take up the nutrients that are present in the soil in the form of compounds soluble in water and weak acids, as well as in the exchangeable state. Conversion of difficultly soluble and insoluble compounds into available ones (mobilization of nutrients) is a continuous process sustained by soil microorganisms and physicochemical and chemical processes*. The mobilization of nutrients in various soils proceeds at different rates, depending on their nature, climatic conditions, soil properties, and the agrotechnical level. If no fertilizers are applied, the soil often lacks the available forms of nutrients, necessary for high yields, that emerge in it during the vegetation period. Therefore, to enhance the effective fertility of soils and crop yields, application of organic and inorganic fertilizers is of paramount importance.

The content of available forms of nutrients, as a function of type of soil, its cultural state, and other factors, may differ not only from one farm to another, but also from field to field at the same farm. This is why agrochemical soil analyses carried out to determine the content of mobile forms of nitrogen, phosphorus, and potassium in combination with field tests are extremely important for correct, differentiated application of fertilizers.

3.5 Absorbing Capacity of Soils

The capacity of the soil to absorb ions and molecules of various substances from solution and to retain them is known as its absorbing capacity. This property of the soil has been known quite long. The first systematic studies into the absorption of salts by soils date back to the middle of the past century. In 1850-1854, the results of experiments were published, stating that the soil absorbs not the entire salt, but only its base, an equal amount of other bases passing from the soil into solution.

The theory of absorbing capacity of soils was further advanced by colloidal chemistry. Many of its concepts and laws

* For more details concerning the content and forms of nutrients and their transformations in the soil, see Chapters 5 through 7.

were put to successful use in studying soil colloids and the absorbing capacity of soils. Noteworthy contributions in this field were made by Gedroits, Wigner, and Mattson. Other important contributions include the research carried out in Pryanishnikov's laboratory on exchange adsorption in soils as related to plant nutrition.

But most of what we know about the absorbing capacity of soils must be credited to Gedroits.

He regarded studies into the absorbing capacity of soils as part and parcel of the theoretical and practical work involving application of fertilizers, plant nutrition, chemical amelioration of soils, and so on. In the following years, many scientists added much to our knowledge of the composition and structure of colloids, the composition and structure of the absorbing complex of the soil, and ion adsorption pattern.

Gedroits distinguished five kinds of absorbing capacity: biological, mechanical, physical, chemical, and physicochemical.

3.5.1 Biological Absorbing Capacity

The biological absorbing capacity is associated with the fact that the soil accommodates living plant roots and microorganisms which selectively absorb nitrogen and ash elements, whereby they are incorporated into the various organic compounds of the hosts. As a consequence, nutrients are prevented from being leached out of the soil. The biological activity in the soil leads to accumulation of organic matter.

Most microorganisms use for their nutrition and building up the same elements as higher plants. The number of microorganisms in the soil is enormous, their total weight reaching several tons per hectare. Microorganisms are especially abundant in the zone of direct contact between the soil and plant roots (rhizosphere).

Using organic substances as a source of nutrients and energy, microorganisms decompose them and convert their constituent nutrients into an inorganic form available to plants. At the same time, they use up a certain amount of nutrients (N, P, S, etc.) to build up their own bodies, convert them into an organic form, and in this sense are competitors of cultivated plants.

A sizable amount of nitrogen, phosphorus, sulphur, and potassium is fixed in the plasma of living microorganisms. E.N. Mishustin's calculations show that the microbial plasma in cultivated soddy podsolic soils contains 125 kg N, 40 kg P_2O_5, and 25 kg K_2O per hectare. When fertilizers are applied, a certain portion of the nutrients they contain is also absorbed by soil microorganisms.

Biological absorption is of crucial importance in the transformations of nitrogen fertilizers in the soil.

Experiments with the stable isotope ^{15}N have shown that fixed in the soil, in an organic form, are 10 to 20 per cent of the nitrogen present in nitrate fertilizers and 20 to 40 per cent of that present in ammonia ones. In spite of the fact that the amount of nitrate nitrogen fixed in an organic form is 1.5 to 2 times as low as that of ammonia nitrogen, biological absorption is particularly important for nitrates and nitrate forms of nitrogen fertilizers. The nitrates not taken up by plants are retained in the soil and prevented from being leached out primarily because they are assimilated by microorganisms, since they are not absorbed in the soil physically, physicochemically, or chemically. It is believed that biological absorption of nitrogen, phosphorus, and other nutrients is a temporary phenomenon in view of the fact that, after microorganisms die away, their plasma undergoes rapid mineralization so that the nutrients it contains are released in an inorganic form and can be utilized by plants.

However, if the soil contains a sufficient amount of readily available organic substances serving as an energy source for microorganisms, they multiply intensively; part of the nitrogen absorbed by them is transferred from one generation to another of the living microflora and is not released in an inorganic form for a long period of time. Besides, when the microbial protein is decomposed and humified, part of the nitrogen fixed in it becomes incorporated into the newly formed humic substances and stays unavailable to plants over a long period of time. If the process of biological absorption of nutrients by microorganisms is too intensive, it may adversely affect the nutrition of cultivated plants. The intensity of biological absorption depends on the moisture content, aeration, and other properties of the soil, as well as on the content and composition of the organic substances in

it, serving as a source of energy for microorganisms. For example, when an organic substance rich in cellulose but deficient in nitrogen (straw or manure with a high straw content) is incorporated into the soil, microorganisms use up the straw as an energy-yielding material and decompose this organic matter to rapidly multiply and to absorb soluble inorganic nitrogenous compounds from the soil solution. As a result, the uptake of nitrogen by plants is adversely affected so that their yield will be low. Similar processes may involve phosphorus, sulphur, and other nutrients necessary for plants.

3.5.2 Mechanical Absorbing Capacity

This type of absorption (adsorption) is due to the capacity of the soil, just as any porous body, to retain small solid particles suspended in the water filtered through it. Notably, after turbid water has passed through the soil, it becomes almost clear because the clay particles suspended in it are mechanically adsorbed in the soil. The mechanical absorbing capacity is responsible for retention of the most valuable colloidal fraction in the soil. Finely divided fertilizers (e.g. ground rock phosphate) applied into the soil are not leached out of its top layer owing to their mechanical adsorption.

3.5.3 Physical Absorbing Capacity

This capacity implies positive or negative adsorption of whole molecules of various substances by soil particles. Physical adsorption is determined mainly by the total surface of solid soil particles. The smaller the size of individual particles, the much larger their total surface. When a cubic centimetre of a substance having a surface of 6 cm^2 is diced into cubes with edge lengths of 10^{-3} and 10^{-6} cm, the total number of the cubes will be 10^9 and 10^{18}, respectively, and the total surface of all cubes will increase from 6 to 6000 and 6 000 000 cm^2. Therefore, the more small particles the soil contains, the greater the total adsorbing surface will be.

If solute molecule are attracted by soil particles with a greater force as compared to water molecules, the concentration of solutes in the film of the solution enveloping the particles will be higher than that at a certain distance from their

surface, and we are dealing with positive molecular (physical) adsorption. This is how molecules of many organic compounds, such as alcohols, organic acids and bases, and high-molecular substances, are adsorbed. According to Gedroits, of all inorganic compounds only alkalis are subject to positive physical adsorption. Soluble mineral salts and inorganic acids, on the contrary, are characterized by negative molecular adsorption. Interaction between a solution of mineral salts and soil particles causes water molecules to be more strongly attracted to their surface, therefore, the concentration of salts in the solution immediately adjacent to the soil particle surface will be lower than in the surrounding solution.

Negative physical adsorption is observed when the soil interacts with solutions of chlorides and nitrates. For example, if dry soil is washed with a $NaNO_3$ solution, the nitrate concentration in the washes will increase rather than decrease. This is due to adsorption of water by the soil, which means that the same amount of the nitrate will be contained within the smaller volume of the filtered liquid.

The negative physical adsorption of chlorides and nitrates is the reason why they are highly mobile in the soil. They move easily through it together with soil moisture. If the moisture content is high, chlorides and nitrates may be leached from plant-free soil into the underlying layers and even into underground water, which must be taken into consideration when applying fertilizers. Such leaching of the Cl^- ion is beneficial because its presence in excess amounts is harmful for plants. This is why, for example, fertilizers with a high chlorine content should better be applied starting with autumn so that at least part of the chlorine could be leached from the arable layer before sowing. Leaching of nitrates is not desirable, hence, nitrate fertilizers should preferably be used in spring, immediately before or at sowing.

3.5.4 Chemical Absorbing Capacity

This kind of absorption is associated with formation of substances completely or almost insoluble in water, as a result of the chemical reactions between individual soluble

salts in the soil. For example, a reaction between soluble ammonium monohydric phosphate with calcium bicarbonate yields poorly soluble calcium diphosphate, and the phosphoric acid anions pass from the soil solution into the solid phase of the soil:

$$(NH_4)_2HPO_4 + Ca(HCO_3)_2 = CaHPO_4 + 2NH_4HCO_3$$

The chemical absorption of certain anions in the soil depends on their capacity to form insoluble or difficultly soluble salts in the interaction with soil ions. The anions of nitric and hydrochloric acids (NO_3^- and Cl^-) do not form any water-insoluble compounds with such common soil cations as Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, Fe^{3+}, and NH_4^+, which is why they cannot be chemically absorbed. Hence, the high mobility of nitrates and chlorides in the soil. The anions of carbonic and sulphuric acids (CO_3^{2-} and SO_4^{2-}) with univalent cations yield soluble salts and, with bivalent cations (Ca^{2+} and Mg^{2+}) predominant in the soil, compounds poorly soluble in water. Therefore, in soils containing large amounts of calcium or magnesium, these anions are chemically absorbed. The anions of phosphoric acid ($H_2PO_4^-$ and HPO_4^{2-}) form with univalent cations readily soluble salts (KH_2PO_4, Na_2HPO_4, $NH_4H_2PO_4$, etc.), while with calcium and magnesium cations they form mono-, bi-, and trisubstituted salts of different solubility. Monocalcium and -magnesium phosphates, such as $Ca(H_2PO_4)_2$, are water-soluble; bisubstituted ($CaHPO_4$) and trisubstituted ($Ca_3(PO_4)_2$) phosphates are poorly soluble. With trivalent aluminium and iron cations, phosphoric acid also forms sparingly soluble compounds.

The chemical absorption of phosphoric acid in soils involves formation of difficultly soluble or insoluble salts with bi- and trivalent cations, i.e. calcium, magnesium, iron, and aluminium. It plays an important role in the transformations of water-soluble form of phosphorus fertilizers in the soils.

In soils with a neutral or weakly alkaline reaction, containing exchangeable calcium or calcium bicarbonate in the soil solution (chernozems, sierozems), the chemical fixation of phosphoric acid and its water-soluble salts results from formation of poorly soluble calcium and magnesium phosphates. For instance, when water-soluble monocalcium phosphate (superphosphate $Ca(H_2PO_4)_2$) is applied into chernozems and

sierozems, the following reactions take place:

$$Ca(H_2PO_4)_2 + Ca(HCO_3)_2 \longrightarrow 2CaHPO_4 + 2H_2CO_3$$
$$Ca(H_2PO_4)_2 + 2Ca(HCO_3)_2 \longrightarrow Ca_3(PO_4)_2 + 4H_2CO_3$$

The water-soluble phosphates may be chemically absorbed also in the interaction with exchangeable calcium:

$$(soil)\ Ca + Ca(H_2PO_4)_2 \longrightarrow (soil)\overset{H}{H} + 2CaHPO_4$$

$$(soil)\overset{Ca}{Ca} + Ca(H_2PO_4)_2 \longrightarrow (soil)\overset{H}{\underset{H}{H}} + Ca_3(PO_4)_2$$

Depending on the amount of water-soluble or exchangeable calcium in the soil, $CaHPO_4$ or $Ca_3(PO_4)_2$ is formed. Bicalcium phosphate ($CaHPO_4$) is soluble in weak acids, hence it is taken up by plants. Tricalcium phosphate is much less readily soluble, therefore, its formation makes phosphoric acid less available to plants. However, when the soil solution is acidified, the difficultly soluble calcium phosphates gradually dissolve. For instance, tricalcium phosphate reacting with the nitric acid resulting from nitrification yields a soluble monocalcium phosphate:

$$Ca_3(PO_4)_2 + 4HNO_3 = 2Ca(NO_3)_2 + Ca(H_2PO_4)_2$$

In acid soddy podsolic and red soils containing many free sesquioxides, the chemical absorption of phosphoric acid proceeds predominantly by way of formation of aluminium and ferric phosphates:

$$Al(OH)_3 + H_2PO_4 \longrightarrow AlPO_4 + 3H_2O$$
$$Fe(OH)_3 + H_3PO_4 \longrightarrow FePO_4 + 3H_2O$$

The freshly precipitated aluminium and ferric phosphates can be taken up by plants; however, in the course of time they crystallize and become less soluble and less readily available. Therefore, phosphoric acid is fixed rather firmly and much more strongly in red and soddy podsolic soils as opposed to sierozems and chernozems.

The intensive chemical absorption of phosphoric acid is responsible for the low mobility of phosphates in the soil and makes the phosphorus of fertilizers less readily avail-

able to plants. Soils can be ranked in the following order of increasing rate of chemical absorption of the soil-derived phosphoric acid: chernozems<sierozems < soddy podsolic soils < red soils.

3.5.5 Physicochemical, or Exchange, Absorbing Capacity

In the interaction between the solid phase of the soil and soil solution physicochemical, or exchange, adsorption is as important as chemical and molecular ones. It is particularly manifest when cations are adsorbed by the solid phase.

The physicochemical, or exchange, adsorption of cations is essentially the capacity of finely divided colloidal soil particles, both mineral and organic, carrying a negative charge, to adsorb various cations from solution. Here, adsorption of some cations is accompanied by the return of an equivalent amount of others (Ca^{2+}, Mg^{2+}, etc.), adsorbed earlier by the solid phase, to the solution. For instance, if a calcium-saturated soil (chernozem) is treated with a potassium chloride solution, potassium cations will be adsorbed by the soil from the latter and, at the same time, the solid phase will give up an equivalent amount of calcium cations to the solution; KCl will be replaced by $CaCl_2$ in it:

$$(\text{soil})\ Ca + 2KCl \longrightarrow (\text{soil})^{K}_{K} + CaCl_2$$

Since what we are dealing with here is cation exchange, adsorption of this kind is termed exchange adsorption, and the capacity of the soil for exchange adsorption reactions is known as **exchange capacity**.

In view of the dual nature of the exchange adsorption reactions, determined by physical and chemical factors, this capacity is also referred to as physicochemical, or colloidochemical, absorbing capacity.

In the case of chemical absorption, reactions between individual salts yield insoluble compounds and result in changes in the composition and overall concentration of the solution, whereas during exchange adsorption the solution concentration remains the same but its composition changes (the solution loses some and gains other cations, the concentration of anions remaining virtually the same).

The physicochemical, or exchange, adsorption of cations plays an important role in soil processes, determines the major physical and physicochemical properties of the soil, such as its structural state, pH, buffering capacity, and is especially important in the interaction of the soil with fertilizers. The transformations of readily soluble fertilizers, particularly nitrogen and potassium ones, in the soil are to a great extent dependent on the processes of physicochemical, or exchange, adsorption.

Each soil in its natural state contains a certain amount of exchangeable cations: Ca^{2+}, Mg^{2+}, H^+, Na^+, K^+, NH_4^+, Al^{3+}, and others.

In most soils, the predominant cation is Ca^{2+} followed by Mg^{2+}; certain soils contain a lot of absorbed H^+ cations and usually lesser amounts of Na^+, K^+, and NH_4^+.

When a soluble salt (e.g. NH_4NO_3, $(NH_4)_2SO_4$, NH_4Cl, $NaNO_3$, KCl, or K_2SO_4) is placed into the soil, its cations are adsorbed from solution by soil particles in exchange for an equivalent amount of cations adsorbed earlier, which are displaced into the solution:

$$\text{(soil) } Ca + (NH_4)_2SO_4 \longrightarrow \text{(soil)}^{NH_4}_{NH_4} + CaSO_4$$

$$\text{(soil) } Ca + 2NaNO_3 \longrightarrow \text{(soil)}^{Na}_{Na} + Ca(NO_3)_2$$

$$\text{(soil) } H + KCl \longrightarrow \text{(soil) } K + HCl$$

The exchange adsorption of cations primarily involves highly dispersed soil particles, both inorganic and organic. Gedroits has termed the totality of highly dispersed soil particles exhibiting exchange capacity the "absorbing complex of the soil".

3.6 Composition and Structure of the Absorbing Complex of the Soil

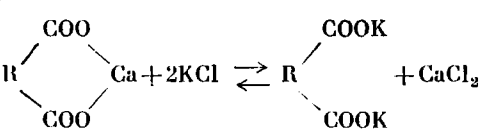
The absorbing complex of the soil is made up of soil colloids, that is, particles smaller than 0.00025 mm and as large as 0.001 mm, exhibiting certain properties typical of colloids, although their physicochemical absorbing capacity is much less pronounced. Soil colloids are subdivided into organic, mineral, and organomineral ones (little is known about

the composition and structure of the latter). Organic colloids are represented mainly by humic substances (humic acids, fulvic acids, and their salts). Mineral colloids include both crystalline compounds, primarily argillaceous minerals (of the kaolinite, montmorillonite, and hydromica groups), and amorphous substances (silicic acid, hydrates of sesquioxides, etc.).

The capacity of organic colloids and argillaceous minerals for exchange adsorption stems from their negative charge. Positively charged are colloidal ferric and aluminium hydroxides. The rest of soil colloids are charged negatively. This is why most soils exhibit a more pronounced capacity for exchange adsorption of cations rather than anions.

In **organic colloids** (humic substances), the negative charge and capacity for exchange adsorption of cations are due to the carboxyls (COOH), which impart them acidic (acidoid) properties, and phenolic hydroxyls (OH); the hydrogen of these groups may be substituted by other cations.

The four carboxyls in the humic acid molecule may dissociate H^+ ions and exchange them for other cations at different pH values: the first H^+ ion is replaced at pH 4.5, the second at pH 7, the third and fourth at pH 9 and above. The hydrogen of phenolic hydroxyls may be displaced by bases only at a highly alkaline pH of the medium. Hence, at acidic and neutral pH values, the exchange adsorption involves only two carboxyls of the humic acid molecule. Their hydrogen is capable of being detached at pH values below 7 and replaced by other cations (e.g. Ca^{2+}) to form the corresponding humates. The bases bound by humic substances may be exchanged for any other cations in the interaction with the soil solution:



Among the **mineral colloids**, negative charge and exchange capacity are displayed by alumosilicate minerals, particularly the secondary (argillaceous) minerals belonging to the kaolinite and montmorillonite groups and hydromicas.

The crystal lattice of argillaceous minerals is composed of

silicon-oxygen tetrahedra consisting of silicon and oxygen atoms, as well as of alumohydroxyl octahedra consisting of aluminium, oxygen, and hydrogen atoms and arranged in a definite pattern with respect to one another. The silicon atom of the silicon-oxygen tetrahedron attach, each, four oxygen atoms to form strongly bound SiO_4 groups of a regular tetrahedral shape. The silicon and oxygen ions in the tetrahedron are arranged as follows: three large oxygen ions lie in a common plane (r 0.132 nm) with the fourth ion above them and the small silicon ion in the centre (r = = 0.039 nm) (Fig. 3.1).

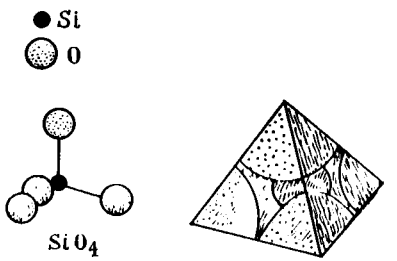
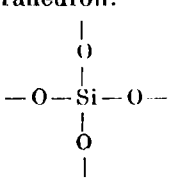


Fig. 3.1: Structure of silicon-oxygen tetrahedra (in two presentations)

If this structure is confined by planes, a tetrahedron will result. The silicon is rather firmly attached to the oxygens, forming a covalent bond. Since silicon is tetravalent and oxygen bivalent, an unsaturated valence remains at each oxygen in the tetrahedron:



hence, each tetrahedron may be regarded as a four-charge anion (SiO_4^{4-}). The excess negative charges can be neutralized by attachment of bases or by joining several tetrahedra together. As individual silicon-oxygen tetrahedra become interlinked via oxygen ions, they form tetrahedral layers, or "sheets", with the result that the free negative valences involved in base binding decrease in number. Notably, when two tetrahedra are joined together, an oxygen becomes common to both. In this case, a $(Si_2O_7)^{6-}$ group emerges, in which 8 positive charges of silicon share 14 negative charges of oxygen, that is, two negative charges less as compared to two separate SiO_4^{4-} tetrahedra,

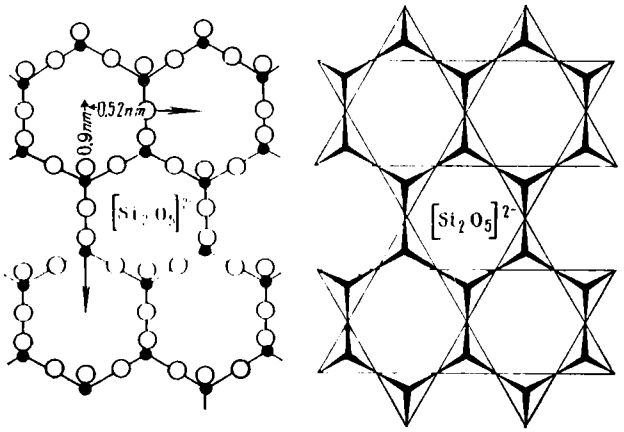
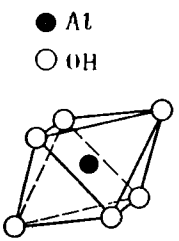


Fig. 3.2: Sheet of silicon-oxygen tetrahedra (in two presentations)



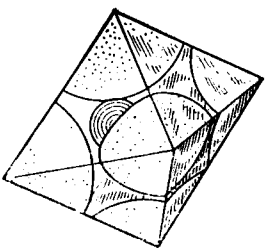


Fig. 3.3: Structure of alumohydroxyl octahedra

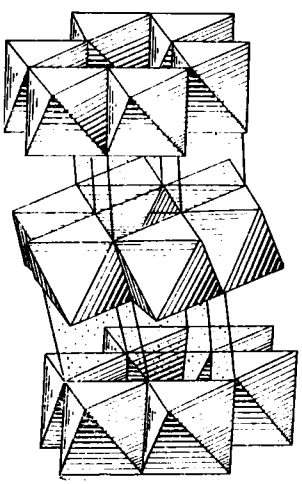


Fig. 3.4: Layers of alumohydroxyl octahedra making up the lattice of gibbsite

Various types of arrangement of silicon-oxygen tetrahedra occur in nature.

In secondary alumosilicate (argillaceous) minerals, these tetrahedra form layers, or "sheets", based on cyclic structures made up of six silicon-oxygen tetrahedra (Fig. 3.2). In such a sheet, every two silicon ions share five oxygen ions, that is, there are 8 positive and 10 negative charges, which is consistent with the formula $(Si_2O_5)^{2-}$. Similar sheets, just as isolated groups of SiO_4^{4-} tetrahedra, are essentially complex anionic compounds in view of the fact that a free valency remains at each oxygen not involved in the joining of two SiO_4^{4-} tetrahedra. The excess negative charges are neutralized as the silicon-oxygen tetrahedral layer is joined with that made up of alumohydroxyl octahedra.

In the latter, the aluminium ion is associated with six hydroxyl ions (OH^-) to form $[(Al(OH)_6]^{3-}$ groups of a regular octahedral shape. The aluminium and hydroxyl ions in such octahedra are arranged in the following manner: the OH^- ions occupy the corners of the octahedron, while the Al^{3+} ions are in the centre (Fig. 3.3).

Since the trivalent aluminium is surrounded by six hydroxyl ions (OH^-), the octahedra also have unsaturated valences and can be joined together forming another layer of the mineral lattice, called octahedral (or gibbsite) layer. Its general formula is $[Al(OH)_3]_n$.

Alumohydroxyl octahedra are interlinked via two hydroxyl ions, each becoming associated with two Al^{3+} ions (dioctahedral structure). Figure 3.4 illustrates the lattice structure of gibbsite, consisting of two parallel octahedral layers.

The crystal lattice of agrillaceous minerals is a combination of silicon-oxygen tetrahedral and alumohydroxyl octahedral layers.

When tetrahedral and octahedral layers are joined together, the O^{2-} ions of the former, occupying the apices of the tetrahedra, become common and bound with the Si^{4+} ions of one layer and the Al^{3+} ions of the other, that is, they serve as "oxygen bridges" interlinking both layers. The resulting structure ("stack") is neutral, the number of the positive silicon and aluminium charges in it being equal to that of the negative oxygen and hydroxyl charges.

No free valences are therefore available for base binding.

Depending on the mineral species, stacks may consist of two or three layers, or "sheets". Their lattice is composed of a plurality of such stacks with interstack spaces in between. Two basic types of lattice structure are distinguished in argillaceous minerals.

In minerals of the **kaolinite group,** a lattice stack consists of two layers interlinked via common oxygen atoms: a layer of silicon-oxygen tetrahedra and an alumohydroxyl octahedral layer (Fig. 3.5).

Minerals of the **montmorillonite group** have a lattice with each stack formed by three layers: one actahedral and two attached tetrahedral ones (Fig. 3.6). The different lattice structure of these two groups of minerals is responsible for their dissimilar properties, particularly absorbing and swelling capacities.

In kaolinites, the distance between the lower part of one stack and that of another is 0.715 nm, while in montmorillonites it is longer and may vary widely (from 0.94 to 2.14 nm) due to contraction or expansion of the interstack space. When moistened, montmorillonites let water into the interstack space and swell considerably.

The emergence of the negative charge in these minerals is associated primarily with the isomorphic substitutions in the silicon-oxygen tetrahedra and alumohydroxyl octahedra of which their lattice is composed. For example, in silicon-oxygen tetrahedral layers, part of the silicon (tetravalent) ions inside the tetrahedra may be isomorphically replaced by aluminium (trivalent) ions with the result that negative charges occur. Schematically, this can be described as follows: a compound of composition $(SiO_2)_n$ is neutral, but substitution of an aluminium for a silicon brings about a negative charge, substitution of aluminium atoms for two silicons results in two negative charges, and so on.

$(SiO_2)_n$	$[(SiO_2)_{n-1}AlO_2]^-$	$[(SiO_2)_{n-2}(AlO_2)_2]^{2-}$
Neutral structure	Structure with one negative charge	Structure with two negative charges

The emerging negative charges are compensated by the corresponding amount of K^+, Na^+, Ca^{2+}, and other cations

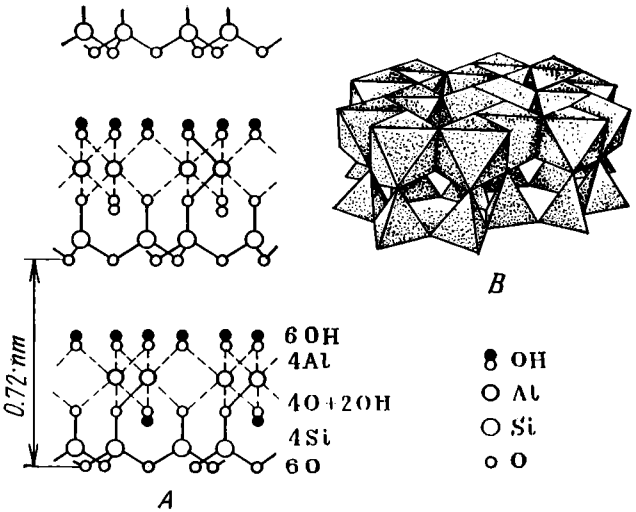


Fig. 3.5: Structure (A) and stack configuration (B) of the kaolinite lattice

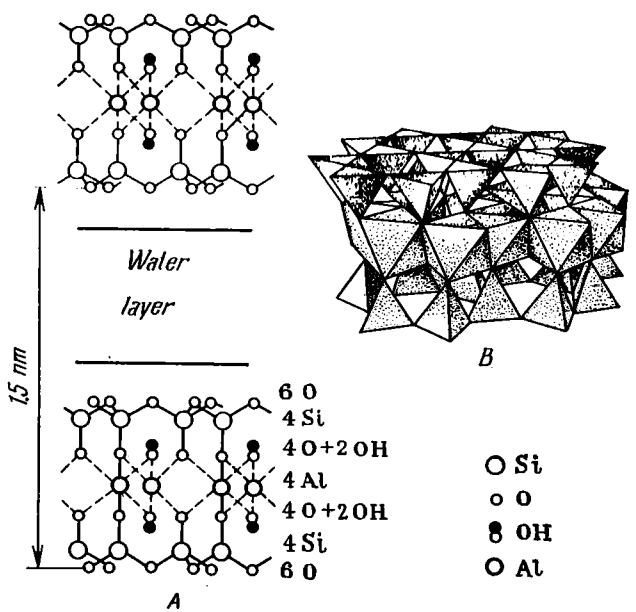


Fig. 3.6: Structure (A) and stack configuration (B) of the montmorillonite lattice

which are capable of dissociation and equivalent exchange for any cations of the soil solution.

Similarly, in alumohydroxyl octahedral layers part of the trivalent aluminium ions inside the octahedra may be replaced by bivalent magnesium ions. In this case, too, negative charges occur to be compensated by calcium ions and other cations. The possibility of substitution of Al^{3+} for Si^{4+} and Mg^{2+} for Al^{3+} in silicate and alumosilicate structures is determined by the radial lengths of these ions.

Cations	Si^{4+}	Al^{3+}	Fe^{3+}	Fe^{2+}	Mg^{2+}	Li^{+}	Na^{+}	Ca^{2+}	K^{+}	NH_4^{+}
Ion radius, nm	0.041	0.050	0.060	0.075	0.065	0.060	0.095	0.099	0.133	0.148

Si^{4+} ions have the shortest radius, followed by Al^{3+}, which is why the silicon ions in a silicon-oxygen tetrahedron may be replaced only by aluminium ions. The radii of the other ions are longer, and they have no room in the tetrahedral space between the four oxygen ions. In alumohydroxyl octahedra, the space between the six hydroxyls is larger, hence, Al^{3+} ions in octahedra can be replaced by some other ions, such as Fe^{3+}, Mg^{2+}, and Li^{+}, whose radii are close in length to that of Al^{3+}. The radii of sodium, potassium, and calcium ions are much longer than those of aluminium or magnesium ions. They cannot substitute for Al^{3+} in an octahedron, to say nothing of Si^{4+} in a tetrahedron, for there is no room for them either in the octahedral or, and especially, in the tetrahedral space. In minerals belonging to the montmorillonite group, the negative charge of the stack results from partial substitution of Al^{3+} for Si^{4+} ions in the two silicon-oxygen tetrahedral layers and partial substitution of Mg^{2+} for Al^{3+} ions in the octahedral layer. The emerging negative charges are compensated by exchangeable cations. Since the interstack spaces in montmorillonites are larger, as compared to kaolinites, and the link between the stacks is weaker, the cations compensating for the negative charge of the stack occupy not only the outer surface of the microcrystalline particles, but also the interstack spaces.

As they interact with salt solutions, the compensating cations occupying the interstack spaces of montmorillonite

microcrystals can be exchanged for salt cations because, during swelling, the solution penetrates the interstack spaces in the lattice. Hence, in minerals belonging to his group, not only the cations on the microcrystal surface, but also those inside the lattice, in interstack spaces, are involved in the exchange. This is what accounts for the higher absorbing capacity of the montmorillonite group minerals.

In minerals of the kaolinite group, isomorphic substitutions are less pronounced. Moreover, the link between their stacks is much stronger, therefore, interaction with the solution and exchange adsorption of cations take place only on the outer surface of microcrystalline particles.

The negative charge of argillaceous minerals not only stems from the isomorphic substitutions in the octahedral and tetrahedral layers, but is also partially due to the oxygen ions localized at the edges of the silicon-oxygen tetrahedral layer, which are linked with a single, rather than two, silicon ion and their second valence remains free for binding a hydrogen ion or a base.

In the case of an acidic reaction (pH $<$ 5), the free valence of the oxygens at the tetrahedral layer edges is occupied by a hydrogen ion that is not capable of dissociation and, therefore, the negative charge results only from isomorphic substitutions in the crystal lattice. At pH values above 6 and especially 7, dissociation of these hydrogen ions and their replacement by other cations may occur because in this case the negative charge and exchange capacity of argillaceous minerals are determined not only by isomorphic substitutions, but also, in part, by the oxygen ions at the edges of tetrahedra. Hence, the exchange adsorption of cations by argillaceous minerals depends on the pH of the medium: at neutral and alkaline pH it is more pronounced than at the acidic pH.

The capacity to adsorb bases becomes especially pronounced in passing from acidic to neutral and alkaline reactions, due to their being bound by the oxygen ions at the edges of tetrahedra in kaolinite group minerals. In those belonging to the montmorillonite group, exchange adsorption is determined predominantly by substitutions in the tetrahedral and octahedral layers of the crystal lattice.

Since, in kaolinites, cations are exchanged only on the outer surface of microcrystals, the cation exchange reactions in this group of minerals proceed at a faster rate, although their absorbing capacity, even at a high degree of dispersion, is much lower as compared to montmorillonites.

The exchange adsorption of cations by various minerals is characterized by the following values (in meq/100 g of the mineral): 3-15 for kaolinite; 5-10, halloysite; 80-120, montmorillonite; 55-65, beidellite; 100-150, vermiculite; and 10-40, illite.

In addition to crystalline colloids (argillaceous minerals) with a negative charge, soils also contain amorphous colloids of aluminium and ferric hydroxides. They exhibit amphoteric properties: depending on the soil solution pH, they may acquire a positive or negative charge, that is, they may behave as bases (basoids) or acids (acidoids). If the solution reacts acid (when the solution contains many H^+ ions and few OH^- ions), the aluminium and ferric hydroxide molecules on the surface of a colloid particle dissociate as bases, giving up OH^- ions to the surrounding solution and becoming positively charged:

$$[Al(OH)_3]_n \rightleftarrows [Al_n(OH)_{3n-1}]^+ + OH^-$$
$$[Fe(OH)_3]_n \rightleftarrows [Fe_n(OH)_{3n-1}]^+ + OH^-$$

When the solution reacts alkaline (high concentration of OH^- ions in the solution), they behave as acids, giving up H^+ ions to the surrounding solution and becoming negatively charged:

$$[Al(OH)_3]_n \rightleftarrows [Al_nO(OH)_{3n-1}]^- + H^+$$
$$[Fe(OH)_3]_n \rightleftarrows [Fe_nO(OH)_{3n-1}]^- + H^+$$

During an intermediate reaction, known as isoelectric point, both types of dissociation will be equivalent; that is, the molecules on the surface of amorphous colloids will give up to the surrounding solution small but equal amounts of cations (H^+) and anions (OH^-), and the colloid will be electroneutral. The isoelectric point of aluminium hydroxide corresponds to pH 8.1, while that of ferric hydroxide, to pH 7.1. In the case of a more alkaline pH, ferric and aluminium hydroxides will exhibit more pronounced acidic (acidoid) properties, whereas at a pH below the isoelectric

point their properties will, on the contrary, be basic (basoid).

In most soils, amorphous colloids of aluminium and ferric hydroxides behave as bases and have a positive charge. The basic properties of these colloids are particularly manifest in acid soddy podsolic and red soils.

Argillaceous minerals of the kaolinite group may also become positively charged at an acidic pH.

The hydroxyl ions linked with aluminium in the octahedral layer on the outer surface of microcrystalline kaolinite particles may be detached at an acidic pH, that is, when H^+ are present in excess amounts in the solution, and positive charges may occur at some portions of a colloid particle.

Thus, minerals belonging to the kaolinite group may be locally charged, at an acidic pH, both negatively and positively. Under such conditions, they are capable of adsorbing anions from the solution in exchange for OH^- ions. Hence, the greater the content of aluminium and ferric hydroxides as well as kaolinite group minerals in the finely dispersed soil fraction, the less pronounced (especially at an acidic pH) is, as a rule, the capacity for exchange adsorption of cations while the capacity for exchange adsorption of anions becomes more manifest.

3.7 Basic Rules Governing Physicochemical, or Exchange, Adsorption of Cations

The exchange reactions between cations adsorbed by the soil and those of salt solutions involve equivalent ratios. When a certain cation is adsorbed by the soil from the solution, the latter receives an equivalent amount of another cation from the soil.

The cation exchange reaction is reversible. After a cation has been adsorbed from the solution (e.g. K^+) and another has been displaced from the soil (e.g. Ca^{2+}), the adsorbed cation may be again displaced into the solution. Therefore, the reaction of exchange adsorption of cations should be written as

$$(\text{soil})\ Ca + 2KCl \rightleftarrows (\text{soil})\begin{matrix}K\\K\end{matrix} + CaCl_2$$

The exchange reaction between cations of the solution and those present in the absorbing complex of the soil ultimately leads to a dynamic equilibrium. The course of the exchange reaction (establishment of the equilibrium) is to a great extent dependent on the composition and concentration of the solution, its volume, the nature of the exchangeable cations, and soil properties. When the solution composition, volume, and concentration change as a result of humidification or desiccation of the soil, application of fertilizers, or formation of mineral salts following decomposition of the organic matter, this equilibrium is shifted so that some cations pass from the solution into the adsorbed state, while the others follow a reverse pathway. For example, when soluble salts (KCl, NH_4Cl, $NaNO_3$, etc.) are incorporated into the soil, the soil solution concentration increases and the salt cations enter into an exchange reaction with those of the absorbing complex of the soil, part of them being adsorbed by the soil. When a cation is taken up by plants, its concentration in the solution goes down and the cation passes from the adsorbed state into the solution in exchange for hydrogen ions or other cations present in the soil solution.

At a constant solution concentration, the amount of cations displaced from the soil into the solution increases with its volume, while at a constant solution volume, the amount of cations displaced from the soil into the solution increases with the concentration of the solution of the displacing salt.

Exchange adsorption reactions in soils obey the law of mass action: the higher the concentration of the displacing cation (e.g. Na^+) in the solution and the lower the content of cations passing into the solution from the soil (e.g. NH_4^+), the greater the amount of the displacing cation adsorbed by the soil. If univalent cations (e.g. Na^+ and NH_4^+) are involved in the exchange, their ratio in the adsorbed state at equilibrium varies with the ratio of the same cations in the solution:

$$\frac{S_{Na}}{S_{NH_4}} = K \frac{[Na]}{[NH_4]}$$

where S_{Na} is the amount of Na^+ adsorbed by the soil, S_{NH_4} is the amount of the NH_4^+ cation in the adsorbed state, [Na]

and $[NH_4]$ are equilibrium concentrations of Na^+ and NH_4^+ cations, respectively, in the solution, and K is a proportionality factor.

When cations of dissimilar valences are exchanged, the relationship between their ratio in the solution and that in the adsorbed state is somewhat more complex. For example, when calcium is displaced from the soil into a sodium salt solution, the ratio between these cations in the adsorbed state is dependent on the Na^+ and Ca^{2+} concentration in the solution in the following manner (E. Gapon's equation):

$$\frac{S_{Na}}{S_{Ca}} = K \frac{[Na]}{\sqrt{[Ca]}}$$

As can be inferred from this equation, an increase in the overall solution concentration leads to a relatively more intensive adsorption of one-charge cations, as compared to two-charge ones, whereas the solution concentration decreases with increasing relative adsorption of two-charge cations.

The cation exchange reactions involved in the interaction between the soil and solution (when the two are related in many aspects) proceed at a fast rate with the equilibrium being established within a few minutes. This can be attributed to the fact that cations are exchanged primarily on the surface of finely dispersed soil particles. Under natural conditions, when the volume of the soil solution is small relative to the solid phase of the soil, it takes more time to achieve full equilibrium in the cation exchange reaction, as was demonstrated by Gorbunov and co-workers. In fact, even under such conditions, the equilibrium sets in (in moist soil) within a short period of time. The exchange reaction rate is responsible for the rapid adsorption, in the soil, of cations brought in with soluble fertilizers (nitrogenous and potassic) in exchange for the cations adsorbed earlier (Ca^{2+}, Mg^{2+}, etc.).

Different cations are adsorbed by the soil and retained in the adsorbed state with dissimilar energy. The greater the atomic mass and charge of the cation, the more intensive its adsorption and the more difficult its displacement from the soil by other cations. Hence, the cation adsorption

energy increases with valence. Bi- and trivalent cations carry more electric charges and, therefore, are more strongly attracted by colloid particles than univalent ones. Within the same valence, the adsorption energy of cations increases with their atomic mass. The only exception among the univalent cations (Li^+, NH_4^+, Na^+, K^+, and Rb^+) is ammonium. Having a lower mass than sodium, it ranks third in terms of adsorption energy.

The increase in the adsorption energy of cations with their atomic mass is due to the decrease in the degree of cation hydration as their atomic mass and size increase. For example, nonhydrated univalent cations have the following radii (in nm): Li^+, 0.078; Na^+, 0.098; NH_4^+, 0.143; and K^+, 0.133, while the same cations with hydration shells have the following radii: 1.003, 0.790, 0.537, and 0.532. The larger an ion without the hydration shell, the smaller it is in the hydrated state. Weakly hydrated cations are more readily attracted by the colloid surface. The presence of a large hydration shell reduces the cation adsorption energy. Therefore, the less a cation is hydrated, the more firmly it is retained by a colloid particle and the more easily it displaces more hydrated (hence, more weakly retained) cations. Cations can be ranged in the following order of increasing absorbing capacity: univalent cations $Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+$; bivalent cations $Mg^{2+} < Ca^{2+} < Co^{2+}$; trivalent cations $Al^{3+} < Fe^{3+}$. The hydrogen ion is an exception. It has the lowest atomic mass but a high adsorption energy and can displace other cations from the absorbing complex. The reason is that, as a hydrogen ion attaches a water molecule in aqueous solutions, it forms a hydroxonium ion, H_3O^+, whose diameter (0.135 nm) is much shorter than that of all other hydrated ions, which is why its adsorption is more intensive as compared to univalent and even bivalent cations. According to Gedroits, the adsorption energy of the hydrogen ion is four times that of calcium and 17 times that of sodium.

Not only different cations but also one and the same cation is adsorbed by the soil and retained there with different forces. For example, when a soil is treated with an NH_4Cl solution, the first portions of the exchangeable cal-

cium it contains are displaced at a relatively fast rate, while the subsequent ones are displaced extremely slowly. As was demonstrated by Gorbunov, 80 to 85 per cent of the total amount of exchangeable cations are displaced from the soil with relative ease, while 15 to 20 per cent are firmly retained in the adsorbed state. The more saturated the absorbing complex of the soil is with a particular cation, the more readily the latter passes into the solution. More readily available to plants are cations that are more easily displaced into the solution from the solid phase of the soil. The different retention and mobility of cations adsorbed by the soil are determined by the composition and structure of the sorbent particles. Different components of the absorbing complex are characterized by different cation retention. As has already been mentioned above, cations are exchanged not only on the surface of colloid particles (extramicellar exchange), but also inside microporous particles (intramicellar exchange). Minerals of the kaolinite group adsorb cations only by the outer surface of the crystal since they have less free space between lattice stacks. In montmorillonites, on the other hand, the free space between stacks is much larger and expands further during swelling, which enables even relatively big ions to penetrate into this space. Intramicellarly adsorbed cations seem to be less readily displaced into the solution in exchange for other cations.

3.8 Non-exchange Adsorption of Cations by the Soil

Some cations may be fixed in the soil in a non-exchangeable form. They include K^+, NH_4^+, Rb^+, and Cs^+. The non-exchange fixation of these cations is associated with their being retained by the crystal lattice of certain minerals. Involved in non-exchange fixation are only argillaceous minerals with a three-layered lattice prone to swelling, such as muscovite, vermiculite, illite, and montmorillonite. Non-exchange fixation resides in penetration of cations into the interstack spaces of the crystal lattice of these minerals. Following its subsequent contraction, the

cations find themselves in closed hexagonal spaces confined by the oxygens of two silicon-oxygen tetrahedral layers.

The non-exchange fixation of NH_4^+ and K^+ in soils varies widely depending on their texture and mineralogical composition. It is more pronounced in chernozems as compared to soddy podsolic ones. Non-exchange fixation increases with the soil profile depth and is more pronounced when humidification of soils alternates with their desiccation. However, even when moist, soils are capable of temporarily fixing K^+ and NH_4^+.

The capacity to fix K^+ and NH_4^+ in a non-exchangeable form is displayed not only by argillaceous minerals, but also by humic substances. The role of the latter in this process, however, is yet to be elucidated. Non-exchangeably adsorbed K^+ and NH_4^+ take more time to become available to plants as compared to exchangeable ones. This is why the uptake of nitrogen and potassium by plants from ammonia and potassium fertilizers incorporated into soils characterized by low capacity for non-exchange fixation becomes somewhat slower. Systematic application of potassium and ammonia fertilizers as well as manure further reduces the capacity of soils to fix NH_4^+ and K^+. Non-exchange fixation is intensified by shallow incorporation of ammonia and potassium salts, when they penetrate soil layers more prone to alternating humidification and desiccation.

3.9 Exchange Capacity and Composition of Exchangeable Cations in Soils

The overall quantity of exchangeable cations adsorbed by the soil is called *exchange capacity*. It is expressed in milligram-equivalents per 100 g of soil.

For example, if 100 g of soil contain 200 mg of calcium, 36 mg of magnesium, and 9 mg of ammonium in an adsorbed state, the exchange capacity of the soil will be $\frac{200}{20} + \frac{36}{12} + \frac{9}{18} = 13.5$ meq/100 g (20 being the equivalent mass of calcium, 12 that of magnesium, and 18 that of ammonium). In the interaction with salt solutions, an

equivalent amount of other cations may be adsorbed by the soil from the solution.

The exchange capacity essentially represents the basic capacity of the soil.

It depends on soil texture, the total content and composition of the fine fraction of the soil. The mineral particles of the soil, having different sizes, are characterized by their capacity for physicochemical adsorption of cations (Table 3.5).

Table 3.5. Exchange Capacity (in meq/100 g of soil) of Various Fractions of Native Rocks

Rock	Particle size (μm)							
	50-10	10-5	5-1	1-0.54	0.54-0.4	0.4-0.28	0.28-0.22	<0.22
Clay cover	8.8	9.2	13.4	45.4	46.3	45.8	52.0	73.0
Loess loam	1.4	1.8	3.0	20.6	—	97.7	98.3	102.0

The exchange capacity of particles exceeding 1 μm in size is insignificant, while that of particles smaller than 1 μm sharply increases. The higher the content of mineral colloid and silt particles (less than 0.001 mm in size), the greater the exchange capacity. Soils of heavy texture with a high content of fine particles (clayey and loamy) have an exchange capacity greater than that of light sandy and sandy-loam soils.

The exchange capacity also depends on the mineralogical composition of the fine soil fraction and the associated adsorbing particle structure. The exchange capacity increases with the content of montmorillonites and hydromicas in the inorganic portion of the soil. When the fine fraction contains great amounts of kaolinites and amorphous ferric and aluminium hydroxides, it is much lower.

Another factor determining the exchange capacity is the humus content of the soil. Humic substances have a much greater exchange capacity than argillaceous minerals. For example, the exchange capacity of humic acids isolated

from various soils (at pH 7) may be as high as 350 to 500 meq/100 g (for montmorillonite it is 80 to 120 meq/100 g and that of kaolinite, 3 to 15 meq/100 g). Therefore, in spite of the preponderance of mineral colloids in the fine fraction, the organic matter is a major factor determining the exchange capacity of soils (Table 3.6).

Table 3.6. Distribution (in %) of the Overall Exchange Capacity Between the Organic and Inorganic Portions of Various Soils (according to Kononova)

Soil portion	Sod podsol			Dark grey	Chernozem				Chestnut	Sierozem
	rich	medium	poor		leached	fertile	ordinary	southern		
Inorganic	71	56	55	39	42	38	45	58	65	52
Organic	29	44	45	61	58	62	55	42	35	48

The higher the humus content, the greater the exchange capacity. In humus-rich chermozems, it is much greater than in soddy podsolic soils. The upper soil horizons containing more organic matter have a greater exchange capacity than the lower ones.

The exchange capacity of humus-rich chernozems is largely determined by their organic portion, while in soddy podsolic soils the determining factor is the inorganic portion.

The cation exchange capacity also depends on soil reaction and the ratio of negatively charged colloids (acidoids) to amphoteric ones (ampholitoids) in the soil.

Negatively-charged organic and most mineral soil colloids become more electronegative at neutral and alkaline pH. Therefore, the lower the concentration of H^+ ions in the solution, the higher the exchange capacity.

The acidic reaction, on the contrary, reduces the negative charge of soil colloids, and the exchange capacity decreases. If a soil is rich in sesquioxides, which are positively charged at pH below 7-8, they will form compounds with negatively charged colloids (acidoids), such as silicic and humic acids,

partially binding their negative charges, whereby the exchange capacity is reduced. At a high content of amphoteric colloids (hydrates of sesquioxides) in the soil and an acidic reaction, its capacity to adsorb anions becomes more pronounced. The smaller the acidoid-to-ampholitoid ratio in the soil and the higher the acidity of the soil solution, the lower the exchange capacity.

The exchange capacity of soils varies with the total content of the fine colloid fraction, the amount and composition of the organic matter, chemical and mineralogical composition of mineral colloid particles, and pH of the soil solution (Table 3.7).

Table 3.7. Exchange Capacity of Some Soils and Humus Content (according to Remezov)

Soil	Percentage content			Exchange capacity (meq/100 g of soil)	Content of exchangeable cations (meq/100 g of soil)		
	humus	mineral particles with a diameter of					
		less than 0.00025 mm	0.00025 to 0.001 mm		$Ca^{2+}+Mg^{2+}$	Na^{+}	
Sod podsol	2.5	2		15	8		7
Grey forest	3	5	4	20	16		4
Chernozem:							
leached	8	15	5	50	40		10
deep	10	5	10	65	60		5
ordinary	6	5	10	35	31	2	2
southern	4.5	5	10	30	28	2	—
Chestnut	2.5	3	5	27	25	2	—
Sierozem	1	3	5	15	14	1	—

The greatest exchange capacity is exhibited by deep chernozems rich in humus. The exchange capacity of soils extending north- and southward from the deep chernozem belt decreases with the humus content. Leached chernozem is especially abundant in mineral colloid and clay particles. Therefore, in spite of the lower humus content, the exchange capacity of this soil approaches that of deep chernozem.

The high exchange capacity of chernozems stems from the high content of organic and mineral colloid particles,

predominance of argillaceous minerals of the montmorillonite group among mineral colloids, and neutral or weakly alkaline reaction. The exchange capacity of soddy podsolic soils is much lower, primarily because of the lower content of organic matter and high content of free sesquioxides in the fine fraction, as well as acidic reaction. The lowest exchange capacity has been observed in sandy loam and sandy soils (5 to 7 meq/100 g), due to the extremely low content of finely dispersed organic and mineral particles in them.

Apart from the exchange capacity, soils also differ in the composition of exchangeable cations. All soils contain calcium and magnesium cations in the adsorbed state. In ordinary and deep chernozems, these cations account for 80 to 90 per cent of the exchange capacity, while hydrogen and aluminium ions are present in small amounts. In southern chernozems, sierozems, and chestnut soils, the predominant cations are calcium and magnesium with little sodium and no hydrogen. In alkaline and saline soils, a lot of sodium is present together with calcium and magnesium in the adsorbed state. In addition to exchangeable calcium and magnesium cations, red and soddy podsolic soils contain hydrogen and aluminium ions (sometimes accounting for 50 and more per cent of the exchange capacity).

Exchangeable potassium and ammonium cations are present in small amounts in all soils.

The exchangeable cation composition determines to a great extent the physical and chemical properties of the soil, crop growth conditions, and fertilizer effectiveness. It also determines the composition of the soil solution. When interacting with soil solutions, exchangeable cations are displaced into the latter (in exchange for cations of soluble salts). If a soil contains a great amount of exchangeable calcium, applied soluble fertilizers (NH_4NO_3, KCl, etc.) will displace predominantly calcium into the soil solution, and if there is little exchangeable calcium but a lot of exchangeable aluminium and hydrogen ions, fertilizers will displace aluminium and hydrogen, whereby the soil solution will be acidified.

The composition of exchangeable cations also affects the state of the absorbing complex of the soil, its particle size

distribution, and hence, the physicomechanical and physicochemical properties of the soil. Cations cause precipitation (coagulation) of negatively charged soil colloids, their coagulating power increasing with charge and atomic mass. Univalent cations exhibit a lower coagulating power than bivalent ones, while that of bivalent cations is lower as compared to trivalent cations. The only exception is the hydrogen ion, approaching bivalent cations in coagulating power.

Cations can be ranged in the following order of increasing coagulating power:

$$Li^+ < NH_4^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < H^+ < Fe^{3+} < Al^{3+}$$

The coagulating power of cations increases with acidity of the medium and decreases when the medium is alkaline. The coagulating effect of univalent cations is less pronounced than the dispersing effect of OH^- ions, which is why at an alkaline pH these cations do not cause coagulation of soil colloids.

On the other hand, the coagulating effect of calcium cations is stronger than the dispersing effect of OH^- ions and, therefore, in a solution containing calcium ions, colloids precipitate even at an alkaline reaction. In this respect, magnesium occupies an intermediate position between univalent cations and calcium, being closer to the latter.

If calcium is predominant among exchangeable cations (e.g. in chernozems), soil colloids are in a coagulated state, which is conducive to formation of water-stable aggregates and improves the soil structure. As calcium precipitates organic and mineral colloids, it enables their retention and accumulation in the soil and enhances its exchange capacity.

Saturation of the soil with univalent cations, particularly sodium, leads to pronounced dispersion of soil colloids and related particles. As a result of dispersion of the fine fraction, the water stability of soil aggregates decreases, the physical properties of the soil deteriorate along with its water and air regimes, and, when moist, such a soil becomes viscous and sticky, whereas desiccation turns it into a hard pan difficult to till. Dispersed organic and mineral colloids are leached out from the soil, whereby it becomes impoverished in terms of nutrients. Moreover, displacement of sodium

from the absorbing complex of the soil into the solution gives rise to sodium bicarbonate, which is responsible for alkaline pH of the solution, detrimental for plant development:

$$(\text{soil})\begin{matrix}\text{Na}\\\text{Na}\\\text{Na}\end{matrix} + Ca(HCO_3)_2 \quad (\text{soil})\begin{matrix}\text{Na}\\\text{Ca}\end{matrix} + 2NaHCO_3$$

When a soil contains large amounts of exchangeable hydrogen and aluminium ions (e.g. soddy podsolic and red soils), many of its properties also deteriorate. Hydrogen ions do not disperse soil colloids, but, as they pass into the adsorbed state, they cause gradual disintegration of the minerals forming part of the absorbing complex of the soil. As a consequence, the soil contains a smaller amount of the colloidal fraction, its structure becomes worse, and the exchange capacity decreases. Besides, aluminium and hydrogen ions pass from the adsorbed state into the solution in exchange for cations of soluble salts. A high concentration of hydrogen and aluminium ions in the solution adversely affects plant development.

The composition and ratio of exchangeable cations in the soil can be controlled by applying fertilizers and ameliorants. For example, liming of soddy podsolic soils displaces hydrogen and aluminium ions from the absorbing complex, while application of gypsum into alkaline soils displaces sodium cations, and the content of exchangeable calcium in these soils increases.

Exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, NH_4^+, etc.) provide a major reserve of nutrients for plants; they are not easily leached but are readily displaced into the solution and taken up by plants.

3.10 Exchange Adsorption of Anions

Highly acidic soddy podsolic and red soils may be characterized by pronounced exchange adsorption of anions as a manifestation of basic (basoid) properties of soil colloids.

The exchange adsorption of anions may be observed either on positively charged colloid particles (colloids of hydrates of sesquioxides) or on positively charged portions

of negatively charged colloids (minerals of the kaolinite group, colloids of proteinaceous nature).

In both instances, anions are adsorbed in exchange for OH^- ions, which are detached at an acidic pH from the molecules localized on the colloid particle surface.

In soils characterized by a weakly acidic, neutral, or alkaline reaction, the exchange adsorption of anions is either insignificant or does not occur at all. This phenomenon is less well known than the exchange adsorption of cations. Investigations have shown that NO_3^- and Cl^- virtually do not lend themselves to adsorption within the range of reactions possible in soils. Only red soils, especially their lower horizons, which are characterized by a highly acidic reaction and a high content of sesquioxides, are capable of adsorbing these anions. The SO_4^{2-} ions were also found to be adsorbed only in red soils, yellow soils, and illuvial horizons of soddy podsolic soils.

Of much greater significance is the exchange adsorption of phosphoric acid anions by the soil. Soddy podsolic soils and even chernozems exhibit a capacity for its exchange adsorption. As regards red soils, which have a propensity for extremely strong fixation of phosphates, it is difficult to tell whether the fixation is purely chemical with formation of insoluble phosphates of sesquioxides or whether it is accompanied by physicochemical, or exchange, adsorption. The exchange adsorption of phosphoric acid anions in soils proceeds primarily by way of their attachment to the positively charged particles of sesquioxides and to that portion of the soil mineral surface which is constituted by sesquioxides (e.g. in kaolinite).

The phosphoric acid anions adsorbed by way of exchange on the surface of colloid particles may be displaced into the solution by other anions of inorganic and organic acids (HCO_3^-, humic acids, etc.). This is why exchangeable phosphoric acid is available to plants.

3.11 Soil Acidity

The soil reaction produces a tangible effect on the development of plants and soil microorganisms, on the rate and direction of the chemical and biochemical processes occurring

in the soil. The uptake of nutrients by plants, the activity of soil microorganisms, mineralization of organic substances, decomposition of soil minerals, dissolution of difficultly soluble compounds, coagulation and peptization of colloids, and other physicochemical processes are strongly dependent on soil reaction. It also influences the effectiveness of applied fertilizers. The latter, in turn, may alter the reaction of the soil solution by acidifying or alkalifying it.

The reaction of the soil solution depends on the ratio of hydrogen (H^+) and hydroxyl (OH^-) ions in it. The concentration of hydrogen ions is usually denoted pH, this symbol being defined as an inverse logarithm of hydrogen ion concentration. Depending on the hydrogen ion concentration and pH value, the following reactions of the soil solution are distinguished:

Reaction	pH	H^+-ion concentration (g/litre)
Strongly acidic	3-4	10^{-3}-10^{-4}
Acidic	4-5	10^{-4}-10^{-5}
Weakly acidic	5-6	10^{-5}-10^{-6}
Neutral	7	10^{-7}
Weakly alkaline	7-8	10^{-7}-10^{-8}
Alkaline	8-9	10^{-8}-10^{-9}
Strongly alkaline	9-11	10^{-9}-10^{-11}

Under natural conditions, the soil solution reaction varies from pH 3-3.5 (in sphagnum peats) to pH 9-10 (in alkaline soils), its typical range being pH 4-8. Characterized by alkaline reaction of the solution are the soils of arid steppes, semideserts, and deserts, such as southern chernozems and chestnut soils (pH 7.5), sierozems ($pH \leqslant 8.5$), and alkaline soils ($pH > 8.5$).

A solution reaction close to neutral (pH 6.5-7) is observed in ordinary and deep chernozems. Leached chernozems and grey forest soils are weakly acidic (pH 5.5-6.5), while soddy podsolic and some peaty soils are acidic or strongly acidic (pH 4-5 and below).

Acid soils occupy vast areas in the USSR and are widely used for cultivation of grain, fodder, vegetable, and industrial crops.

The response of most farm crops and useful soil microorganisms to increased acidity is negative. Therefore, it is impor-

tant to elucidate the nature of soil acidity and to find ways to eliminate it.

Distinction is made between two kinds of soil acidity: actual (or active) and potential (or latent), the latter being subdivided into exchange and hydrolytic acidities.

3.11.1 Actual Acidity

By definition, actual acidity implies acidity of the soil solution, due to increased concentration of H^+ ions in it as compared to OH^- ions.

CO_2 formation in the soil is an incessant process. Dissolution of carbon dioxide in soil moisture yields H_2CO_3 which dissociates into H^+ and HCO_3. As a result, the hydrogen ion concentration in the solution increases (the solution becomes acidified). The CO_2 content in the soil air and solution is in the following ratio to pH of the solution:

CO_2 content in soil air (vol.%)	0.03	0.3	1.0	3.0	10.0	100
CO_2 in soil solution (mg/litre)	0.5	5.4	17.9	54.0	178.7	1787.0
Solution pH	5.7	5.2	4.9	4.7	4.5	3.9

Therefore, the higher the CO_2 concentration in soil air, the more of it is dissolved in soil moisture and the more acidic the solution becomes.

However, the carbonic acid forming in the soil solution is neutralized by exchangeable bases (Ca, Mg, Na) and by calcium and magnesium carbonates. The reaction between carbonic acid and calcium carbonate or an absorbing complex saturated with calcium yields soluble calcium bicarbonate:

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2$$

$$(soil)\ Ca + 2H_2CO_3 = (soil)^{H}_{H} + Ca(HCO_3)_2$$

If the soil contains exchangeable sodium, sodium bicarbonate or carbonate may form in the solution:

$$(soil)\ Na + H_2CO_3 = (soil)\ H + NaHCO_3$$

$$(soil)^{Na}_{Na} + H_2CO_3 = (soil)^{H}_{H} + Na_2CO_3$$

Calcium and sodium carbonates undergo hydrolytic decomposition in the solution, whereby an extremely weak

carbonic acid and strong bases emerge:

$$Ca(HCO_3)_2 + 2H_2O = Ca(OH)_2 + 2H_2CO_3$$
$$NaHCO_3 + H_2O = NaOH + H_2CO_3$$
$$Na_2CO_3 + 2H_2O = 2NaOH + H_2CO_3$$

The hydroxyl ion concentration increases in the solution, and it becomes alkaline. The alkalization of the solution is particularly strong by sodium carbonate, not as strong by sodium bicarbonate, and weak by calcium and magnesium bicarbonates. This is why sodium carbonates form in the solution of soils containing a lot of exchangeable sodium (alkaline and saline soils), and the soil solution becomes alkaline. When a soil contains calcium and magnesium carbonates with calcium being predominant among the exchangeable cations (sierozems, chernozems), the main compound forming in the soil solution is calcium bicarbonate, which is a weaker alkalifying agent for these soils, and their solution has a weakly alkaline or neutral reaction (pH 7-8).

In soils where hydrogen ions are present among exchangeable cations along with calcium and magnesium (leached chernozems, grey forest and soddy podsolic soils), the reaction of the soil solution is determined by the total content in it of carbonic acid, calcium bicarbonate, and soluble organic acids and their salts. The reaction of the solution in these soils depends on the composition of exchangeable cations and varies within a pH range of 5 to 7. The lower the calcium content in the absorbing complex and the higher that of hydrogen ions, the less calcium bicarbonate will be present in the soil solution, the free H_2CO_3 content going up and the pH value going down.

In acid and highly acidic soddy podsolic and peat-bog soils, containing a small amount of exchangeable calcium and many hydrogen and aluminium ions, the soil solution is acidified not only by carbonic acid, but also by soluble organic acids and aluminium salts whose hydrolysis yields an acid and a weak base. In this case, the soil solution is acidified to pH 4.5 and below.

Thus, actual acidity is the acidity of the soil solution due to carbonic acid (H_2CO_3), *water-soluble organic acids, and* ***hydrolytically acid salts.*** It can be determined by measuring

the pH value of a water suspension or extract from a soil. Actual acidity bears directly on the development of plants and soil microorganisms.

3.11.2 Exchange Acidity

Apart from actual acidity, soils are also said to have a potential (latent) acidity due to the presence of exchangeable hydrogen or aluminium ions. Part of the adsorbed, or exchangeable, hydrogen ions may be displaced into the solution by cations of neutral salts. For example, if a soil is treated with KCl solutions, potassium cations will be adsorbed by it, and hydrogen ions will pass from the absorbing complex into the solution:

$$(\text{soil})\ \text{H} + \text{KCl} = (\text{soil})\ \text{K} + \text{HCl}$$

As a result of this displacement of hydrogen ions, the soil solution is acidified. This type of soil acidity is referred to as exchange acidity. In addition to exchangeable hydrogen, highly acidic mineral soils contain exchangeable aluminium, which is also capable of passing into the solution during interaction of the soil with neutral salts:

$$(\text{soil})\ \text{Al} + 3\text{KCl} = (\text{soil})\text{K}_3 + \text{AlCl}_3$$

In the solution, aluminium chloride undergoes hydrolytic dissociation yielding a weak base and a strong acid:

$$\text{AlCl}_3 + 3\text{H}_2\text{O} = \text{Al(OH)}_3 + 3\text{HCl}$$

The acid resulting from displacement of aluminium from the soil during its treatment with a neutral salt solution plus the exchangeable hydrogen passing into the salt extract are responsible for exchange acidity of the soil. Thus, exchange acidity is the acidity due to exchangeable hydrogen and *aluminium ions extractable from the soil with a neutral salt solution.*

The question as to the nature of exchange acidity, or rather, which of the exchangeable cations, hydrogen or aluminium, are predominant in acid soils and responsible for this acidity, has long been debated.

At present, as a result of numerous investigations, it

is considered most likely that, in the interaction of acid soils with solutions of neutral salts, both hydrogen and aluminium ions pass into the salt extract. The ratio between the two depends on the soil formation conditions, composition of the absorbing complex, and some other factors. Notably, organic colloids of the soils contain primarily exchangeable hydrogen, while the exchange acidity of the inorganic fraction is determined by both hydrogen and the aluminium passing into the salt extract.

Exchange acidity is typical of soddy podsolic and red soils as well as soils of the northern part of the chernozem zone. In soils characterized by a weakly acidic reaction of the water extract, exchange acidity is insignificantly low, disappearing completely in alkaline soils. It regulates the reaction of the soil solution. When the solid phase of the soil interacts with cations of soluble salts resulting from mineralization of organic substances or cations introduced into the soil with inorganic fertilizers, exchangeable hydrogen and aluminium ions pass into the solution and enhance the actual acidity, and if the soil solution is neutralized, it is acidified again owing to exchange acidity.

Exchange acidity gains in importance when large amounts of soluble inorganic fertilizers are incorporated into the soil. While readily becoming active and acidifying the soil solution, it adversely affects the development of plants and soil microorganisms sensitive to acidity. Aluminium is especially toxic for many plants. Therefore, when acid soils are limed, not only actual but also exchange acidity must be neutralized.

Exchange acidity is expressed in terms of the pH value of a KCl extract or in milligram-equivalents per 100 g of soil. It also comprises actual acidity, hence, exchange acidity is always higher than the actual one, and the pH value of a salt extract is always lower than that of a water extract if the soil has exchange acidity.

3.11.3 Hydrolytic Acidity

When a soil is treated with a neutral salt solution, not all adsorbed hydrogen ions pass into solution, that is, the entire potential acidity is not manifest in this case. To

displace hydrogen ions from the absorbing complex of the soil more completely one should treat it with a normal solution of a hydrolytically alkaline salt, such as sodium acetate (CH_3COONa). This salt is hydrolyzed in an aqueous solution to yield weakly dissociating acetic acid and a strong base, which renders the solution alkaline (pH $\approx$ 8.2).

$$CH_3COONa + H_2O \rightleftarrows CH_3COOH + NaOH \longrightarrow CH_3COOH + Na^+ + OH^-$$

The alkaline reaction of the solution of this salt is the main reason why the exchangeable hydrogen is expelled from the soil to a greater extent.

During interaction between the sodium acetate solution and absorbing complex of the soil, hydrogen ions are displaced into the solution in exchange for sodium cations and combine with the remaining hydroxyl ions, resulting in H_2O molecules that do not lend themselves easily to dissociation:

$$(soil)\ H + CH_3COOH + Na^+ + OH^- \longrightarrow (soil)\ Na + CH_3COOH + H_2O$$

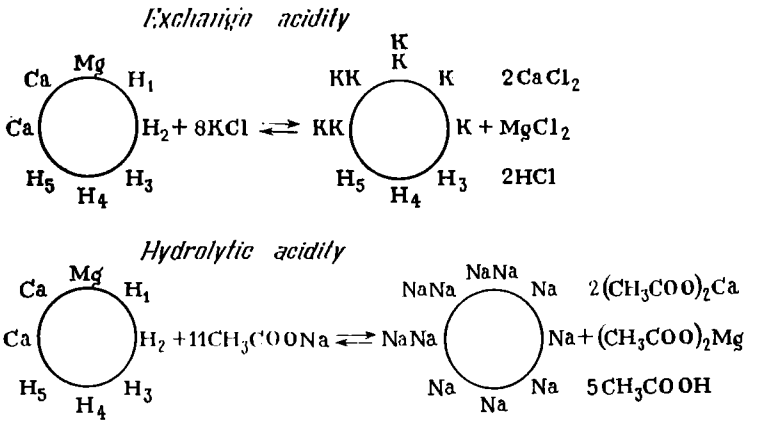
The greater the number of sodium ions adsorbed by the soil and that of combined hydroxyl ions, the larger the amount of the acetic acid forming in the solution. Its quantity can be determined by titrating the solution with an alkali. This type of soil acidity, manifesting itself through a hydrolytically alkaline salt, is known as **hydrolytic acidity**. It involves the less mobile portion of adsorbed hydrogen ions that are less readily exchangeable with the soil solution cations.

The absorbing complex of the soil contains hydrogen ions capable of being replaced by bases at different pH values.

The hydrogen ions that are bound in soil colloids can be exchanged for bases at a weakly acidic reaction (pH 5.5-6) and may be displaced from the absorbing complex of the soil into the solution by cations of a neutral salt. These hydrogen ions (along with exchangeable aluminium ions) are responsible for exchange acidity of the soil. Other adsorbed hydrogen ions, that dissociate less readily, can be exchanged for bases only in neutral and alkaline media. They are not exchanged for bases as easily and can be dis-

placed into the solution only by a hydrolytically alkaline salt.

The relationship between exchange and hydrolytic acidities can be represented schematically as follows (according to Remizov):



The hydrogen ions present in the absorbing complex of the soil have subscripts in increasing order of difficulty with which they are replaced by salt cations.

The effect of a neutral salt solution (at a given exchange acidity) is such that exchanged for bases are only a few H^+ ions, for example H_1 and H_2, the rest of the hydrogen ions not entering into exchange reactions. Under the effect of the alkaline sodium acetate solution (at a given hydrolytic acidity), the substitution of hydrogen ions in the absorbing complex is more complete.

The acidity of a soil treated with a CH_3COONa solution is much more pronounced than exchange acidity. Taken into account in this case is the overall acidity of the soil, including both actual and potential (exchange and purely hydrolytic) acidities (in the last case, hydrogen ions are not displaced by KCl but by a 1 *N* CH_3COONa). Hence, hydrolytic acidity is, in fact, the acidity of the soil solution after treatment of the soil by sodium acetate and involving all hydrogen ions present in the soil, including not only

highly mobile (exchange) ions, but also the less mobile ones capable of being replaced by bases only at an alkaline reaction.

Hydrolytic acidity is expressed in milligram-equivalents per 100 g of soil. Sometimes, determination of hydrolytic acidity gives lower results than that of exchange acidity, primarily because acetic acid anions are sorbed by certain soils, in which colloids with pronounced basoid properties are predominant (red soils), in exchange for the displaced OH^- ions with the result that the acidity of the soil extract is lower.

Obviously, the traditional method of determining hydrolytic acidity is not suitable in such cases.

Soils become hydrolytically acidic as soon as they start losing bases. As the loss of bases becomes more tangible, they also acquire exchange and actual acidity.

All chernozems, with the exception of southern ones, exhibit hydrolytic acidity, although exchange acidity is not always present in them. If a soil has exchange acidity, it should be regarded as part of hydrolytic acidity. Leached chernozems, poorer in bases, are characterized by both hydrolytic and, to some extent, exchange acidity. Soddy podsolic soils, which contain even less bases, display pronounced hydrolytic acidity, marked exchange acidity, and also actual acidity.

Since hydrolytic acidity involves the less mobile hydrogen ions, it is less harmful for plants (in the absence of exchange acidity). Knowledge of the amount of hydrolytic acidity is extremely important for practical purposes (liming, application of ground phosphate rock).

3.11.4 Degree of Base Saturation of the Soil

The reaction of the soil solution depends not only on the exchange and hydrolytic acidity, but also on the saturation of the soil with bases. If hydrolytic acidity of the soil is denoted by H, while the total amount of exchangeable bases (Ca, Mg, K, Na, etc.) is designated as S, their sum gives the overall exchange capacity of the soil (T) in meq/100 g:

$$S + H = T$$

The sum of exchangeable bases (S), expressed as percentage of the exchange capacity (T), is known as the **degree of base saturation of the soil** and denoted by V:

$$V \quad \frac{S}{T} \cdot 100, \quad \text{or} \quad V = \frac{S}{S+H} \cdot 100$$

The degree of saturation indicates the relative contributions of exchangeable bases and hydrolytic acidity to the overall exchange capacity. It is an important characteristic of the absorbing capacity and acidity of the soil (Fig. 3.7).

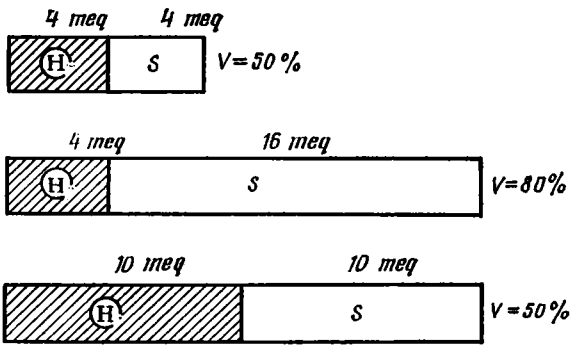


Fig. 3.7: Ratio between exchange capacity, hydrolytic acidity, and degree of base saturation

If the hydrolytic acidity of two soils is the same and equal to 4 meq/100 g but the exchange capacity of the first soil is 8 and that of the other 20 meq, then, in the first soil, corresponding to 4 meq of hydrolytic acidity are only 4 meq of exchangeable bases, and its degree of base saturation is 50 per cent, while, in the second soil, 16 meq of exchangeable bases correspond to the same 4 meq of hydrolytic acidity, and its degree of base saturation is 80 per cent. In spite of the same hydrolytic acidity the first soil is comparatively more acidic because of the lower degree of base saturation. It is in a greater need to be deacidified, for example by liming, than the second soil whose acidity accounts for only a small portion of the entire exchange

capacity. The third soil has the same degree of base saturation (50%) as the first, yet their exchange capacity and hydrolytic acidity are different. In spite of the same degree of base saturation, the third soil with its higher hydrolytic acidity requires more lime for its pH value to be equalized with that of the first soil.

3.11.5 Buffering Capacity of the Soil

The reaction of the soil solution does not remain constant. Biological, chemical, and physicochemical processes in the soil lead to the formation of acids or bases, whereby the reaction varies. The release of carbonic acid, formation of nitric acid as a result of nitrification and other acidic products as a result of activity of soil microorganisms tend to acidify the soil solution.

The soil reaction also changes due to fertilizers. For instance, application of physiologically acidic salts (NH_4Cl, $(NH_4)_2SO_4$, etc.) acidifies the soil solution, while application of physiologically alkaline salts ($NaNO_3$, $Ca(NO_3)_2$) neutralizes or alkalizes it. During systematic application of physiologically acidic or physiologically alkaline fertilizers, the reaction of the soil solution may vary widely and affect the development of cultivated plants and soil microorganisms.

However, changes in the solution pH, caused by the above factors, will differ from one soil to another, being less pronounced in some soils and more pronounced in others. The capacity of a soil to withstand changes in soil reaction towards more acidic or alkaline pH is called **buffering capacity**. It depends essentially on the buffering properties of the solid and liquid phases. The buffering capacity of the soil solution is determined by the constituent weak acids (H_2CO_3, water-soluble organic acids) and their salts. Weak acids (e.g. H_2CO_3) dissociate incompletely, therefore, they will be present in the solution mainly in the form of nondissociated molecules with only a small amount being dissociated completely:

$$\underset{\text{major portion}}{H_2CO_3} \rightarrow \underset{\text{small portion}}{H^+ + HCO_3^-}$$

If an alkali appears in a soil solution containing carbonic acid, H^+ ions become bound yielding weakly dissociating H_2O molecules, the equilibrium shifts, and some of the acid molecules dissociate. The H^+ ions will combine with some OH^- ions of the added alkali to form H_2O, and pH of the solution will change but insignificantly. Hence, the weak acid will prevent the solution from being alkalized. For example, when $Ca(OH)_2$ forms in the soil (after application of physiologically alkaline calcium nitrate), it will react with carbonic acid, yielding insoluble calcium carbonate and water without any perceptible alkalinization of the solution:

$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O$$

A solution containing a mixture of a weak acid and its salt (e.g. H_2CO_3 and $Ca(HCO_3)_2$) will also act as a buffer against acidification. The salt of the weak acid dissociates almost completely [$Ca(HCO_3)_2 \rightarrow Ca^{2+} + 2HCO_3^-$]. According to the law of mass action, dissociation of a weak acid (H_2CO_3) depends on the amount of its anions (HCO_3^-) present in the solution and varies inversely with their concentration:

$$\frac{[H^+] \cdot [HCO_3^-]}{H_2CO_3} = K, \text{ hence, } [H^+] = K\frac{[H_2CO_3]}{[HCO_3^-]}$$

In a solution containing both H_2CO_3 and $Ca(HCO_3)_2$, the concentration of HCO_3^- anions depends mainly on the content of calcium bicarbonate. Therefore, in the presence of such a salt, a large amount of anions form in the solution, inhibiting dissociation of the acid which is already weak, part of H^+ ions is converted from a dissociated to non-dissociated state, and their concentration in the solution decreases with increasing salt concentration. If, say, nitric acid appears (as a result of nitrification) in a soil solution containing H_2CO_3 and $Ca(HCO_3)_2$, its reaction with calcium bicarbonates yields weakly dissociating carbonic acid; that is, combining with HCO_3^- anions, hydrogen ions become undissociated, a neutral salt and a weakly dissociating acid form in the solution, whereby changes in pH will be insignificant, and the solution will act as a buffer against acidification:

$$Ca^{2+} + 2HCO_3^- + 2H^+ + 2NO_3^- = Ca^{2+} + 2NO_3^- + 2H_2CO_3$$

Besides, when soil air contains small amounts of CO_2, the resulting carbonic acid dissociates into water and carbon dioxide ($H_2CO_3 = CO_2 + H_2O$). This is why formation of nitric acid through nitrification in the presence of calcium bicarbonate does not lead to heavy acidification of the soil solution by virtue of its buffering properties.

A similar effect is produced by a buffer system consisting of organic acids and their salts:

$$(RCOO)_2Ca + 2HNO_3 = \underset{\text{weakly dissociating acid}}{2RCOOH} + Ca(NO_3)_2$$

$$2RCOOH + Ca(OH)_2 \longrightarrow R(COO)_2Ca + 2H_2O$$

The buffering capacity depends not only on the soil solution composition, but also on the properties of the solid phase of the soil. The role of the buffering properties of the soil solution in the overall buffering capacity of the soil is usually insignificant. A much more important factor is the solid phase of the soil, primarily its colloidal portion. The buffering capacity of the soil depends mainly on the content and composition of exchangeable cations in its absorbing complex. The higher the exchange capacity of a soil, the more pronounced its buffering properties. Acting as buffers against acidification are exchangeable bases (Ca, Mg, etc.). If an acid appears in a base-saturated soil (e.g. H_2SO_4 as a result of ammonium sulphate application), hydrogen ions of the acid are exchanged for cations of the absorbing complex (hydrogen becomes exchangeable, and a neutral salt forms in the solution), and the reaction of the soil solution varies but slightly:

$$\begin{matrix} Ca \\ (soil)Ca \\ Mg \end{matrix} + 2H^+ + SO_4^{2-} \longrightarrow \begin{matrix} H \\ H \\ (soil)Ca \\ Mg \end{matrix} + CaSO_4$$

The greater the degree of base saturation of the soil and the higher its overall exchange capacity, the greater its resistance to acidification. Acidification of the soil solution is also mitigated by carbonates ($CaCO_3$ and $MgCO_3$) since they neutralize acids yielding bicarbonates:

$$2CaCO_3 + H_2SO_4 = CaSO_4 + Ca(HCO_3)_2$$

Therefore, base-saturated soils (chernozems and especially calcareous soils) exhibit pronounced buffering properties as regards acidification.

Soils not saturated with bases and containing sizable amounts of exchangeable hydrogen and aluminium ions (soddy podsolic and red soils) act as buffers against alkalinization. When an alkali is introduced into such soils, its cations are absorbed in exchange for H^+ ions with water forming as a result:

$$(\text{soil})\begin{matrix}\text{H}\\\text{Ca}\end{matrix} + \text{Ca(OH)}_2 = (\text{soil})\begin{matrix}\text{Ca}\\\text{Ca}\end{matrix} + 2\text{H}_2\text{O}$$

The higher the hydrolytic acidity of a soil, the more pronounced its buffer action against alkalinization. However, soils containing small amounts of bases are poor buffers against acidification, because the acids forming in them are not completely neutralized by the bases.

The capacity of the soil to withstand changes in the soil solution reaction is important in application of inorganic fertilizers. In soils with weak buffering properties (sandy and sandy loam soils, as well as most humus-deficient soddy podsolic soils), sharp changes in pH are possible after application of acidic fertilizers, which may adversely affect the development of plants and soil microorganisms. In heavy and humus-rich soils with pronounced exchange and buffering capacities, the shift in pH of the soil solution is insignificant even at high rates of acidic and alkaline fertilizer application. Especially resistant to acidification of the solution are soils with a high degree of base saturation, while soils with a low degree of saturation are resistant to alkalinization. Systematic application of organic fertilizers in combination with liming enhances the exchange capacity and degree of base saturation of the soil to increase its buffering capacity.

3.12 Agrochemical Characteristics of Main Soil Types in the Soviet Union

Soddy podsolic soils are characterized by an acidic reaction (pH 4-4.5) and pronounced exchange acidity (1-2 meq/100 g) with exchangeable Al accounting for 80 to 90 per cent of

its value and hydrolytic acidity (3-6 meq/100 g), while their exchange capacity (5-15 meq) and degree of base saturation (30-70%) are low. Most of these soils require liming.

Soddy podsolic soils typically contain small amounts of humus, total nitrogen and phosphorus, decreasing sharply with depth. The agrochemical properties of these soils vary widely depending on their texture and state of cultivation. Loamy soils contain 2 to 4 per cent of humus, 0.1 to 0.2 per cent of nitrogen, 0.07 to 0.12 per cent of phosphorus (P_2O_5), and 1.5 to 2.5 per cent of potassium (K_2O). The reserves of humus (in the 0-20 cm layer) range from 60 to 80 tons, those of nitrogen, from 3 to 6 tons, phosphorus, from 2 to 3.5 tons, and potassium, from 45 to 75 tons per hectare. Sandy and sandy loam soils are poorer in humus, N, P, K, Ca, Mg, and micronutrients, as compared to loamy ones. The humus content in light soils does not exceed 0.5 to 1.0 per cent, the nitrogen content being 0.03 to 0.08 per cent, that of phosphorus being 0.03 to 0.6 per cent, and that of potassium, 0.5 to 1.0 per cent. The reserves of these components are as follows: humus, 15 to 30 tons; nitrogen, 0.9 to 2.4 tons; phosphorus, 0.9 to 1.8 tons; and potassium, 15 to 30 tons per hectare. The content of micronutrients in soddy podsolic soils varies widely, some being deficient (B, Mo, etc.), others present in excess amounts (e.g. Mn).

Most soddy podsolic soils are also characterized by a relatively low content of available (inorganic) forms of nitrogen, mobile phosphorus, and, in the case of sandy and sandy loam soils, potassium. The amount of acidity and content of mobile forms of nutrients in soils are to a great extent dependent on their state of cultivation (Table 3.8).

The higher the state of cultivation of these soils (with systematic application of organic and inorganic fertilizers), the lower the acidity, the greater the contents of humus, total nitrogen, mobile phosphorus, and exchangeable potassium, and the better their fertility.

Since soddy podsolic soils are usually deficient in nutrients but are sufficiently moist, application of organic and inorganic fertilizers is highly effective. The most effective, hence highly recommended, inorganic fertilizers are nitrogen ones and also, for soils with a low state of cultivation, phospho-

Table 3.8. Agrochemical Characteristics of Soddy Podsolic Soils

State of cultivation	pH of salt extract	Arable layer thickness (cm)	Humus content (%)	Mobile phosphorus	Exchangeable potassium
				mg/100 g of soil	
Low	4-4.5	up to 20	1.5-2	up to 5	up to 10
Medium	4.6-5.0	20-22	2-3.5	5-10	10-15
High	5.1-6.0	22-25	2.5-4	15-25	20-30

rus fertilizers. The most effective for sandy and sandy loam soils are potassium and magnesium fertilizers.

Grey forest soils are characterized by a weakly acidic reaction (pH 4.8-6), low exchange (up to 1 meq) but high hydrolytic acidity (from 2 to 6 meq per 100 g), exchangeable bases in an amount of 15 to 30 meq with Ca constituting 80 to 90 per cent, and a degree of base saturation equal to 80 to 85 per cent. The humus content in the arable layer (0-20 cm) varies from 2 to 6 per cent, its total amount ranging from 60 to 150 tons per hectare and decreasing with depth more gradually than in soddy podsolic soils. The total content of nitrogen in these soils is 0.15 to 0.35 per cent, that of phosphorus 0.05 to 0.2 per cent, and that of potassium, 1.5 to 3 per cent. The reserves of these nutrients in the 0-20 cm layer are 4.0 to 10, 1.5 to 6, and 45 to 90 tons per hectare, respectively.

Depending on the humic layer thickness, humus content, and degree of podsolization, grey forest soils are subdivided into light grey, grey, and dark grey types with different agrochemical properties (Table 3.9).

From light grey to grey and on to dark grey soils, the humic layer thickness, humus content, total exchangeable bases, and degree of base saturation increase, while acidity decreases. Grey forest soils usually contain small amounts of available compounds of nitrogen, mobile phosphorus and potassium, but their content may vary widely depending on the state of cultivation of the soil and the amount of fertilizers it had received previously.

Table 3.9. Agrochemical Characteristics of Grey Forest Soils

Type	Humic layer thickness (cm)	Humus content (%)	pH of salt extract	Hydrolytic acidity	Total exchangeable bases	Degree of base saturation (%)	Mobile phosphorus	Mobile potassium
				meq per 100 g			mg per 100 g	
Light grey	15-25	1.6-3.4	4.8-5.4	2.3-3.8	10-18	72-82	6	10
Grey	25-30	2.2-4.7	5.2-5.7	2.9-3.5	14-25	76-87	8	13
Dark grey	40-60	3.5-7.0	5.5-6.0	2.3-5.4	20-36	80-86	12	15

Such soils call for systematic application of organic and inorganic fertilizers, liming being also necessary for light grey soils with an acidic reaction. Inorganic fertilizers are particularly effective in the western provinces of the grey forest soil zone, their effectiveness dropping eastwards.

Crop yields on grey forest soils are enhanced primarily by nitrogen fertilizers, followed by phosphorus and potassium ones, the latter being necessary for potato, sugar beet, and high yields of grain crops.

Chernozems. The agrochemical properties of major subtypes of chernozems are summarized in Table 3.10.

As opposed to other soils, chernozems are characterized by a higher natural fertility, have a rather thick humic layer, contain a lot more humus (4-12%) and total nitrogen (0.2-0.5%) in the arable layer with a gradual decrease in their contents with depth. The reserves of humus and nitrogen in the 0-20 cm layer are 60 to 220 and 3 to 15 tons per hectare, respectively, these amounts being three to four times greater in a metre-deep layer. The total content of phosphorus (P_2O_5) varies from 0.1 to 0.3 per cent, its reserves being 2 to 4.5 tons per hectare. The reaction of these soils is close to neutral or weakly alkaline (pH 6-8), the exchange acidity is virtually nil, and the hydrolytic acidity ranges from 0 to 4 meq per 100 g. Chernozems exhibit high exchange capacity (30-60 meq) and degree of base saturation (85-100%). Typical chernozem is characterized by the thickest humic layer (100-180 cm), higher contents of humus (8-12%), total nitrogen (0.4-0.5%), and phosphorus (0.25-0.35%) with correspondingly high reserves of these nutrients (120-220,

Table 3.10. Agrochemical Characteristics of Chernozems

Subtype	Humic layer thickness (cm)	Humus content (%)	pH of water extract	Hydrolytic acidity
				meq per
Leached	80-150	6-9	5.5-6.5	2-4
Typical	100-180	8-12	6.5-7	0.5-3
Ordinary	60-140	5-8	7-8	0-1
Southern	40-80	3-6	7-8	0-0.5

7-15, and 3.5-4.5 t/ha, respectively) as well as exchange capacity (50-60 meq per 100 g). These figures are lower to the north, in leached chernozem, and to the south, in ordinary and, particularly, southern chernozems. Weakly acidic reaction is typical of leached chernozem (pH 5.5-6.5), while weakly alkaline reaction (pH 7.8) is observed in ordinary and southern chernozems which are also characterized by a higher degree of base saturation and negligible hydrolytic acidity. The hydrolytic acidity of leached chernozems may often be as high as 3 to 4 meq per 100 g. All subtypes of chernozem are rich in potassium whose total content is 2.5 to 3 per cent and reserves are 75 to 90 tons per hectare. In spite of the high natural fertility of chernozems, they usually contain small amounts of available nitrogen and mobile phosphorus, which is especially true in the case of old-arable and weakly fertilized soils. This is why these soils are best improved by phosphorus and, under favourable moisture conditions, nitrogen fertilizers. Old-arable and weakly fertilized chernozems contain smaller amounts of total and exchangeable potassium, as compared to virgin ones, therefore, such soils call for potassium fertilizers (along with nitrogen and phosphorus ones) to be applied under potassium-loving crops (sugar beet, potato, sunflower, etc.). Inorganic fertilizers are most effective in the more humid western regions of the chernozem belt, their efficiency decreasing eastwards with decreasing humidity.

Chestnut soils are subdivided into dark chestnut, chestnut, and light chestnut soils (Table 3.11).

Exchange capacity	V (%)	Reserves in 0-20 cm layer (t/ha)			
100 g		humus	N	P_2O_5	K_2O
45-55	85-95	100-160	5-9	3-4	45-55
50-60	90-98	120-220	7-15	3.5-4.5	50-60
40-50	95-100	80-140	5-7	3-4	50-55
25-35	98-100	60-110	3-6	2-3.5	50-60

Dark chestnut soils mark the transition from chernozems to chestnut soils. They are characterized by a humic layer thickness of 35 to 45 cm, a humus content of 4 to 5 per cent, a total nitrogen content of 0.2 to 0.3 per cent, and a phosphorus content of 0.1 to 0.2 per cent with a gradual decrease with depth. The calcareous horizon lies at a depth of 45 to 50 cm. The reaction of this soil is weakly alkaline (pH 7-7.2), and the content of total exchangeable cations ($Ca^{2+} + Mg^{2+}$) is 30 to 35 meq per 100 g. The content of readily soluble salts is low, and they occur at depths below 2-2.5 m.

Table 3.11. Agrochemical Characteristics of Chestnut Soils

Subtype	Humic layer thickness (cm)	Humus (%)	Total N (%)	Total phosphorus (%)	pH of salt extract	Total exchangeable cations
Dark chestnut	35-45	4-5	0.2-0.3	0.1-0.2	7-7.2	30-35
Chestnut	30-40	3-4	0.15-0.2	0.1-0.2	7.2-7.5	20-13
Light chestnut	25-30	2-3	0.1-0.15	0.8-0.15	7.4-8	12-15

Chestnut and light chestnut soils occurring in the more arid regions of dry steppes are characterized by a thinner humic layer (30-40 and 25-30 cm), lower contents of humus (3-4 to 2-3%) and total nitrogen (0.15-0.20 and 0.10-0.15%) with a more pronounced decrease with depth. The calcareous

horizon is higher (effervescence under the effect of HCl at depths of 30-40 and 5-30 cm), and the reaction is weakly alkaline to alkaline (pH 7.2-8). The total content of exchangeable bases is 20 to 35 and 12 to 15 meq per 100 g, the predominant exchangeable cation being Ca^{2+} followed by Mg^{2+} and, in light chestnut soils, Na^{+}. There are many alkali and alkali-affected variants of the latter. Chestnut soils are characterized by different degrees of salinity; however, the salic horizon usually lies at a depth of one metre and below. Water-soluble salts are leached out of the top layer, their content (primarily Ca and Mg bicarbonates) being low (hundredths of a per cent). The predominant water-soluble salts in the salic horizon are sulphates and chlorides. Chestnut soils abound in potassium but are deficient in mobile forms of nitrogen and phosphorus. Yet, because of lack of moisture in these soils, the effectiveness of inorganic fertilizers is usually low. In dry farming, small doses of phosphorus fertilizers are recommended to be drilled while planting grain crops. In irrigation farming, the effectiveness of nitrogen and phosphorus fertilizers sharply increases, but potassium ones remain ineffective. Gypsum application is recommended to enhance the fertility of alkalized soils.

Sierozems are subdivided into three subtypes: light, typical (ordinary), and dark. Cultivation of these soils involves irrigation (only dark sierozems can be cultivated without irrigation).

Sierozems are characterized by pronounced calcareousness, and low humus and nitrogen contents. The humus content in the 0-20 cm layer is 1 to 1.5 per cent in light sierozems, 1.5 to 3 per cent in typical sierozems, and 4 to 5 per cent in dark ones. The total nitrogen content is, respectively, 0.07 to 0.22, 0.1 to 0.2, and 0.35 to 0.4 per cent. The humus reserves in the same layer range from 30 to 40 tons per hectare in light sierozems and 120 to 150 tons in dark sierozems, while the nitrogen reserves are 2 to 4 and 8 to 10 tons per hectare, respectively.

The total content of phosphorus is 0.08 to 0.2 per cent and its reserves, 2 to 6 tons per hectare, the respective figures for potassium being 2.5 to 3 per cent and 75 to 90 tons per hectare, that is, the reserves of phosphorus and potassium in these soils are substantial.

Sierozems have a weakly alkaline reaction (pH 7.2-8) and a relatively low exchange capacity (9-10 meq per 100 g in light sierozems, 12-15 meq in typical sierozems, and 18 to 20 meq in dark ones). Ca^{2+} accounts for 80 to 98 per cent, Mg^{2+} for 10 to 15 per cent, and K^+ and Na^+ for 5 to 8 per cent of the total exchangeable cations. Irrigated sierozems are characterized by high biological activity and nitrification capacity, but the forming nitrates tend to migrate intensively (during watering) across the soil profile. To improve the fertility of these soils, it is extremely important to systematically apply organic and inorganic fertilizers.

The most effective inorganic fertilizers are nitrogen ones followed by phosphorus fertilizers, which are highly effective when the soil contains little mobile phosphorus. Sierozems are more abundant in potassium than in nitrogen and phosphorus. However, long-irrigated soils used for cultivation of cotton and other crops also require potassium fertilizers, especially when nitrogen and phosphorus fertilizers are applied systematically at high rates.

Chapter 4

Chemical Amelioration Techniques. Application of Lime and Gupsum

Most of the territory of the USSR is occupied by acid and alkaline soils. The presence of large amounts of exchangeable hydrogen and aluminium ions in acid soils and sodium cations in alkaline soils is highly detrimental insofar as the physical, physicochemical and biological properties of these soils, to say nothing of their fertility, are concerned. Their radical improvement calls for chemical amelioration in combination with other soil management practices.

The techniques of chemical amelioration of acid and alkaline soils are based on changing the composition of exchangeable cations, primarily by introducing calcium into the absorbing complex of the soil. Liming is the most widely used way to neutralize the acidity and improve the fertility of acid soils, while the high alkalinity of alkaline soils and their properties are controlled by application of gypsum.

4.1 Liming of Acid Soils

Lime fertilizers have been used from time immemorial. Farmers of Gaul and the British Isles used marl and chalk to fertilize fields, meadows, and pastures two millennia ago. In the 16th through 18th centuries, lime fertilizers were widely applied in the countries of Western Europe. However, not knowing at that time exactly what lime does to the soil, farmers regarded it as a mere substitute for manure and tended to apply lime in large quantities and too often, which sometimes produced negative results.

Liming as a means to control soil acidity became standard practice only at the turn of the century.

The potentialities of liming had long attracted the attention of Russian scientists. As far back as the early 19th

century, Pavlov described at length liming practices, aimed at improving soil quality, in his books *Farming Chemistry* (1825) and *A Course in Farming* (1837). In his dissertation "Liming of Soils" (1865), Stebut emphasized its importance in enhancing crop yields on soddy podsolic soils.

The first exact field experiments to elucidate the efficiency of lime were conducted under Mendeleev's supervision in 1867-69. In the years that followed, similar experiments were carried out by Engelgardt, Kostychev, Kossovich, Gedroits, Pryanishnikov, and other scientists. Liming was used with great success at agricultural experimental stations.

More extensive and carefully planned experiments with liming of acid soils were undertaken in this country after the Great October Socialist Revolution. This research is still under way at many institutes and experimental stations.

These studies have given insight into the action of lime on the soil, established its high effectiveness when used on acid soddy podsolic soils, and led to development of techniques for most efficient application of lime fertilizers. Liming has become a widely used practice in socialist agriculture.

During the tenth five-year plan period (1975-80), more than 32 million hectares of acid soils were treated with lime.

According to the statistics of the State Agrochemical Service, more than 50 million hectares of arable lands and about 13 million hectares of meadows in the USSR are highly acidic ($pH < 5.5$). Most of the acid soils are soddy podsolic. In addition, liming has been found to be necessary for peat-boggy, grey forest, and red soils. The acid soddy podsolic soils of the Non-Black Earth zone are deficient in organic matter and nutrients, and their fertility is poor. Even after application of organic and inorganic fertilizers, such soils are unable to sustain high yields of most crops without liming. This is why, in the resolution "On Measures for the Further Development of Agriculture in the Non-Black Earth Zone of the RSFSR", adopted by the CPSU Central Committee and the Council of Ministers of the USSR, emphasis is placed on liming of acid soils, as a decisive factor of increased agricultural production.

4.1.1 Response of Crops to Soil Reaction and Liming

Most crops and soil microorganisms thrive when the soil reaction is weakly acidic or neutral (pH 6-7); the effect of alkaline and excessively acidic reactions on them is adverse. Various plants respond differently to soil reaction or, in other words, they differ in the pH range, favourable for their growth and development, and to departures of the reaction from the optimum (Table 4.1).

Table 4.1. Response of Various Plants to Soil Reaction

Plant	pH range favourable for growth	Plant	pH range favourable for growth
Alfalfa	7.2-8.0	Lettuce	6.0-7.0
Sugar beet	7.0-7.5	Sunflower	6.0-6.8
Hemp	6.7-7.4	Cotton	6.5-7.3
Cabbage	7.0-7.4	Millet	5.5-7.5
Cucumber	6.4-7.5	Rye	5.0-7.7
Onion	6.4-7.5	Oat	5.0-7.5
Barley	6.0-7.5	Buckwheat	4.7-7.5
Winter wheat	6.3-7.5	Radish	5.0-7.3
Spring wheat	6.0-7.3	Carrot	5.6-7.0
Maize	6.0-7.5	Tomato	5.0-8.0
Soybean	6.5-7.5	Flax	5.5-6.5
Pea	6.0-7.0	Potato	4.5-6.3
Fodder bean	6.0-7.0	Tea	4.0-5.0
Kidney bean	6.4-7.1	Lupine	4.6-6.0
Clover	6.0-7.0	Rutabaga	4.8-5.5
		Timothy	4.5-7.6

According to their response to soil reaction and liming, plants can be divided into several groups:

1. The plants most sensitive to acidity include cotton, alfalfa, sainfoin, sugar, table and fodder beets, hemp, and cabbage. They grow well only on soils with neutral or weakly alkaline reactions (pH 7-8) and respond vigorously to liming even in the case of weakly acidic soils.

2. Next in sensitivity to high acidity are barley, spring and winter wheats, maize, soybean, kidney bean, pea, fodder bean, clover, sunflower, cucumber, onion, and lettuce. They grow better on soils with weakly acidic or neutral

reaction (pH 6-7) and respond well to liming of not only highly but also moderately acidic soils. After liming, the yield of these crops perceptibly increases, the mortality of winter wheat and clover sharply decreasing during winter.

3. Rye, oat, millet, buckwheat, timothy, tomato, radish, and carrot are less sensitive to high acidity. These crops grow normally within a broad pH range, on soils with acidic and weakly alkaline reactions (pH 4.5-7.5), weakly acidic reaction (pH 5.5-6) being the most favourable for their growth. They respond positively to liming of highly and moderately acidic soils at full rates, which is explained not only by reduced acidity, but also by more intensive mobilization of nutrients and improved nutrition of plants with nitrogen and ash elements.

4. Flax and potato require liming only when grown on highly acidic soils.

The potato is tolerant to acidic pH and grows well on acid soils. Flax is characterized by a narrow optimal pH range. It is sensitive to increased soil acidity and to alkaline reaction. Weakly acidic soils (pH 5.5-6) are the most favourable ones for its growth.

At high rates of liming and after reducing the soil reaction to neutral pH, the yield of potatoes and flax is adversely affected along with their quality, potatoes being affected by scab and flax, by bacteriosis.

The negative effect of heavy liming on these crops is due not so much to neutralized acidity as to the decreased content of available boron compounds in the soil as well as excess calcium ions in the soil solution, resulting in reduced uptake of other cations, such as magnesium and potassium, by the plants.

5. Blue and yellow lupines, seradella, and tea grow better on acid soils (optimal pH 4.5-5.0) and worse on soils with alkaline and even neutral reaction. These crops are sensitive to excess amounts of water-soluble calcium in the soil, especially at the early stages of growth, which is why they respond negatively to high liming rates. However, if magnesium-containing lime fertilizers are applied at lower rates, no reduction in the yield of these crops is observed.

Different sensitivity to acidity and responses to liming are displayed not only by different farm crops, but also

different varieties of most crops (especially barley, spring wheat, maize, pea, clover, and alfalfa). For example, experiments have shown that varieties of southern origin, developed on soils with neutral reaction, are more sensitive to acidity and, when grown on acid soddy podsolic soils, respond better to liming than northern varieties developed on acid soils.

The effect of acid reaction on plants is manifold. The direct adverse effect of increased hydrogen ion concentration in the soil is combined with the indirect negative effect of certain conditions and factors associated with the acid reaction.

High acidity of the soil solution suppresses the growth and branching of roots, adversely affects the physicochemical state of the cytoplasm of root cells and their permeability, whereby the uptake of soil and fertilizer nutrients by plants is reduced.

When the soil solution is highly acidic, hydrogen ions penetrate plant tissues in large quantities and acidulate the cell sap. Because of the pronounced buffering properties of the cytoplasm and cell sap, the reaction of the solution in plant tissues changes to a much lesser extent than that of the external solution. However, depending on the degree of acidulation of the medium, changes in pH may be significant and produce a tangible effect on the biochemical processes occurring in the plant.

If the reaction is acidic, the synthesis of proteinaceous substances is inhibited, the content of proteins and total nitrogen in plants decreases, while the amount of nonproteinaceous forms of nitrogen increases, and the conversion of monosaccharides into other more complex organic compounds is suppressed.

Plants are particularly sensitive to soil acidity at the initial stage of their growth, immediately after sprouting. At later stages, they are relatively more tolerant to acidic pH (Table 4.2).

At the initial stage of growth, acidic reaction seriously upsets carbohydrate and protein metabolism and adversely affects the initiation of generative organs, which has a remote effect on fertilization and grain forming with subsequent reduction in yield.

Table 4.2. Response of Barley Plants to Acidic Soil Reaction at Different Stages of Growth (according to Avdonin)

pH during plant growth	Grain yield	
	g/pot	%
6.5-7 throughout the vegetation period	9.44	100.0
5.0-5.5 throughout the vegetation period	4.37	46.3
5.0-5.5 within the first 20 days and 6.5-7.0 throughout the rest of the vegetation period	4.91	53.0
5.0-5.5 within the second 20 days and 6.5-7.0 throughout the rest of the vegetation period	9.02	95.6
5.0-5.5 within the third 20 days and 6.5-7.0 throughout the rest of the vegetation period	7.67	81.3
5.0-5.5 within the fourth 20 days and 6.5-7.0 throughout the rest of the vegetation period	9.23	97.8

Apart from the direct negative effect produced on plants by high hydrogen ion concentration, soil acidity also exerts a multiple indirect influence. As hydrogen displaces calcium from the soil humus, it increases its dispersity and mobility, whereas saturation of colloidal particles with hydrogen leads to their eventual breakdown. This is why acid soils contain a small amount of the colloidal fraction, hence, their poor physical and physicochemical properties, inferior structure, low exchange and buffering capacities. The microbiological processes beneficial for plants are suppressed in acid soils, the formation of available nutrients being inadequate.

Various soil microorganisms respond differently to soil acidity. Mold fungi thrive at pH 3-6 and may grow even at higher acidity. Fungi include many parasitic and pathogenic species. Soil acidity promotes their development. At the same time, many useful soil microorganisms develop better at neutral and weakly alkaline pH. The optimal pH values for nitrifiers, free-living nitrogen-fixing bacteria, nodule bacteria of alfalfa, pea, and other legumes range from 6.5 to 7.5. At higher acidity, the vital activity of nitrogen-fixing and nitrifying bacteria is suppressed, and at pH below 4-4.5 many of them cannot develop at all. Therefore, fixation of air nitrogen in acid soils is strongly inhibited or discontinues altogether, mineralization of the organic matter

slows down, the nitrification process is suppressed, and, ultimately, the conditions of nitrogen nutrition go from bad to worse. In acid soils, mobile forms of phosphorus combine with sesquioxides to form insoluble and unavailable aluminium and iron phosphates, and mineralization of organic phosphorus compounds is less intensive, whereby phosphorus nutrition of plants is also adversely affected. At high acidity, molybdenum converts into less soluble forms and becomes less available to plants. Plants grown on highly acidic sandy and sandy loam soils may also become deficient in calcium and magnesium.

The adverse effect of high acidity is largely due to increased solubility of aluminium and manganese compounds in the soil. Their high content in the soil solution inhibits plant development to an even greater degree than excess of hydrogen ions.

The negative effect of aluminium on most plants becomes manifest already at a concentration of 2 mg per litre of the solution. Higher aluminium concentrations sharply reduce the yield of crops and even kill the plants. Excess of aluminium affects primarily the root system (Figure 4.1) Roots become much shorter, coarse, dark, and slimy, their hairs decreasing in number. Excessive uptake of aluminium and manganese upsets the carbohydrate, nitrogen and phosphate metabolism in plants and negatively affects the initiation of reproductive organs as well as grain forming. Therefore, the negative effect of excess amounts of these elements is more pronounced on generative as opposed to vegetative organs. Plants are especially sensitive to mobile forms of aluminium and manganese at the initial stage of their growth and during wintering. Their excess amounts in the soil sharply reduce the winter hardiness of winter crops, clover, and alfalfa, and most plants die.

Increased concentrations of mobile aluminium are tolerated only by a few plants, while most species die at the same concentrations. Avdonin classifies plants into the following four groups in terms of their sensitivity to aluminium: the first group, which is characterized by marked tolerance to aluminium, includes oat and timothy; the second, less tolerant group, includes lupine, potato, maize, and millet; the third group of highly sensitive plants includes

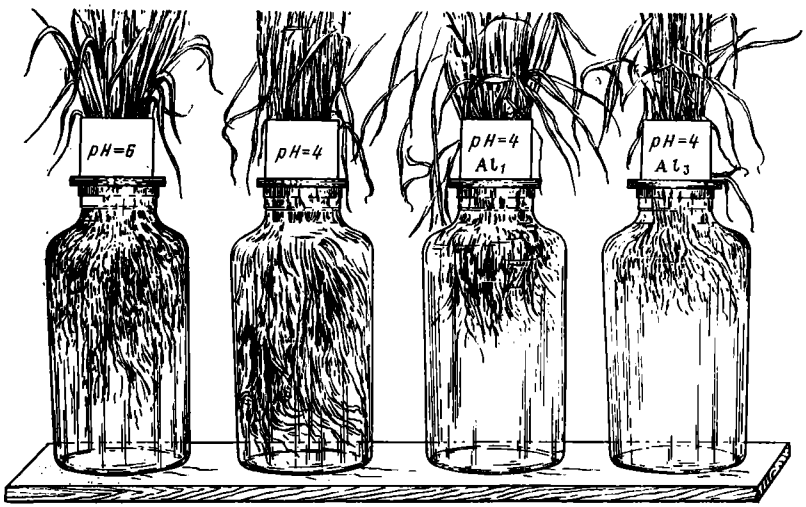


Fig. 4.1: Effect of aluminium on the root system of plants. Experiment with wheat in water cultures. The first aluminium rate (Al_1) in 2 mg/litre and the second (Al_3), 6 mg/litre of solution

flax, pea, kidney bean, buckwheat, barley, and spring wheat; and the fourth group consists of plants most sensitive to aluminium, such as table and sugar beets, clover, alfalfa, winter wheat, and winter rye (during wintering). Clover starts being inhibited already at a mobile aluminium concentration of two and more milligrams per 100 g of soil, its mortality increasing sharply at concentrations of 6 to 8 mg per 100 g of soil.

The sensitivity of plants to the acidic pH of the medium, on the one hand, and that to mobile forms of aluminium, on the other, are not always in a strict relationship. Some plants do not tolerate soil acidity (maize, millet) but are relatively resistant to aluminium, while others (flax) grow well on an acid soil but are highly sensitive to aluminium. The different sensitivity of plants to mobile forms of aluminium stems from their dissimilar capacity to immobilize them in roots. More tolerant to aluminium are plants capable of immobilizing it in the root system with the result that

aluminium does not reach growing points and generative organs.

It is often impossible to distinguish between the negative effect on plants of mobile forms of aluminium and manganese in the soil and that of a high hydrogen ion concentration in the soil solution. At high contents of mobile aluminium and manganese compounds in the soil, the deleterious effect of acidity on plants is much more pronounced.

The effect of high soil acidity on plants depends not only on plant characteristics, but also on the composition and concentration of other cations in the soil solution, nutrient content in the soil, and other soil properties. High concentrations of calcium cations in the solution slow down the absorption of hydrogen and aluminium ions by roots, and their negative effect is mitigated. In the presence of calcium, plants can withstand a more acidic reaction.

Another factor that minimizes the negative effect of high acidity is an adequate supply of plants with phosphorus. Systematic application of phosphorus fertilizers reduces the content of mobile iron and aluminium compounds in the soil because of their becoming insoluble products of the reaction with phosphoric acid. The protective action of phosphorus also stems from the fact that it renders H^+ and Al^{3+} in plants themselves less toxic. When plants are adequately supplied with phosphorus, more aluminium is immobilized in roots without being transported to growing points and generative organs. Moreover, phosphorus promotes root development, carbohydrate and nitrogen metabolism in plants, initiation of generative organs, and grain forming, thereby mitigating or neutralizing the adverse effect of high concentrations of H^+, Al^{3+}, and Mn^{2+} ions in the solution.

The high sensitivity of plants to soil acidity and increased concentration of Al^{3+} and Mn^{2+} ions in the soil solution at the beginning of growth is mainly due to reduced uptake of phosphorus. Improvement of phosphorus nutrition at this stage (by drilling application of phosphorus fertilizers) alleviates the harmful influence of high H^+ and Al^{3+} ion concentrations on the young plants. When the basic nutrients (NPK) are deficient, the effect of high soil acidity on the growth and yield of crops becomes more pronounced,

while their adequate supply minimizes this effect. High acidity adversely affects the yield of plants sensitive to acidic reaction even when all nutrients are in sufficient quantities, but when they are in short supply, the decrease in yield becomes dramatically high. Hence, the negative effect of soil acidity on plants may be more or less pronounced depending on various factors.

Environmental conditions may shift the above-mentioned optimal pH ranges for different plants (Table 4.1) towards more acidic or alkaline values. Yet the differences between individual plants, as regards their sensitivity to soil acidity, persist. Most plants are adversely affected by high soil acidity, both directly and indirectly. To ensure high and stable yields of farm crops and to enhance the effectiveness of fertilizers incorporated into acid soils, their high acidity must be neutralized by liming.

4.1.2 Interaction of Lime with the Soil

Lime ($CaCO_3$) is virtually insoluble in pure water (one part (by weight) of the carbonate dissolves in 100 thousand parts of water). However, its solubility increases perceptibly (almost 60-fold) in water containing carbon dioxide. Lime incorporated into the soil gradually transforms to soluble calcium (or magnesium) bicarbonate under the effect of the carbon dioxide present in the soil solution:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

Calcium bicarbonate dissociates into Ca^{2+} and $2HCO_3^-$ ions and is partially hydrolyzed:

$$Ca(HCO_3)_2 + 2H_2O = Ca(OH)_2 + 2H_2O + 2CO_2$$
$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

The concentration of Ca^{2+} and OH^- ions increases in a soil solution containing calcium bicarbonate. Calcium cations displace hydrogen ions from the absorbing complex of the soil, and the acidity is neutralized:

$$(\text{soil})\begin{matrix}H\\H\end{matrix} + Ca^{2+} + 2HCO_3^- \longrightarrow (\text{soil})\ Ca + 2H_2CO_3$$

$$(\text{soil})\begin{matrix}H\\H\end{matrix} + Ca^{2+} + 2OH^- \longrightarrow (\text{soil})\begin{matrix}Ca\\H\end{matrix} + 2H_2O$$

Lime also interacts with free humic and other organic acids in acid soils, as well as with the nitric acid forming in the course of nitrification, and neutralizes them:

$$2RCOOH + CaCO_3 \longrightarrow R(COO)_2Ca + H_2O + CO_2$$

$$2HNO_3 + CaCO_3 \quad Ca(NO_3)_2 + H_2O + CO_2$$

Application of lime at full rates eliminates actual and exchange acidities, minimizes hydrolytic acidity, raises the calcium content in the soil solution, and increases the degree of base saturation of the soil.

The speed and completeness of action on the soil reaction and base saturation depend on the rate and form of the applied lime fertilizer. The higher the $CaCO_3$ rate, the greater its impact on acidity and base saturation of the soil (Table 4.3).

Table 4.3. Effect of Various Liming Rates on Soil Properties (according to the USSR Research Institute of Fertilizers and Agronomical Soil Science)

Parameter	Lime rates in fractions of hydrolytic acidity				
	0	1/3	2/3	1	2
pH of water extract	4.4	5.0	5.8	6.5	6.9
Hydrolytic acidity (meq/100 g)	5.5	3.4	1.9	1.1	0.9
Degree of base saturation (%)	47.3	65.3	82.2	89.7	95.6
Exchangeable calcium (meq/100 g)	4.4	4.8	5.6	6.0	7.6
Water-soluble calcium (meq/100 g)	23.0	30.0	35.0	40.0	48.0

While neutralizing acidity, liming also affects many other soil properties, creating a favourable medium for plant growth and development of useful microorganisms. The lime-derived calcium coagulates soil colloids, improves soil structure, and increases the water stability of soil aggregates. Lime also improves water permeability and aeration, prevents crusting, and facilitates cultivation of heavy soils.

Liming at appropriate rates minimizes the content of mobile compounds of aluminium, iron, and manganese in the soil; they pass into an insoluble form, whereby their harmful effect on plants is eliminated.

Free-living nitrogen-fixing and nodule bacteria become more active in limed soils, whereby the soil is enriched with atmospheric nitrogen.

Limed soils provide a better environment for nitrifiers, intensify mineralization of organic nitrogen compounds to ammonia and its nitrification, and promote accumulation of nitrate nitrogen. As a result, the nitrogen nutrition of plants improves, particularly within the first few years after liming.

Liming suppresses noxious microorganisms and prevents infestation of plants with various diseases. However, application of lime at increased rates may activate not only useful but also some harmful microorganisms causing plant diseases.

Liming also intensifies mobilization of soil phosphates and improves phosphorus nutrition of plants. This is due to the activation of bacteria mineralizing organic phosphates and to conversion of difficultly soluble iron and aluminium phosphates into more readily available calcium phosphates as a result of neutralization of soil acidity. The positive effect of liming on the increase in the amount of available phosphorus in the soil is slow and continues for many years. In an experiment conducted at the Dolgoprudny agrochemical station, the content of mobile phosphorus in the soil had been increasing under the effect of liming for at least 24 years.

During liming, the potassium of difficultly soluble minerals passes into more mobile compounds. However, because of the antagonism between calcium and potassium, its uptake by plants does not increase.

Another effect of liming is changes in the mobility and availability of soil micronutrients. Liming of acid soddy podsolic soils converts molybdenum compounds into more readily available forms, whereby the uptake of this nutrient by plants improves. Boron and manganese compounds, on the contrary, become less readily available, and plants may suffer from their deficiency. As a result, liming fails to produce the desired effect and may even reduce the yield or affect the quality of some crops (flax, potato, lupine). Application of boron fertilizers enhances the effectiveness of liming and eliminates the negative effect of high lime rates on the yield and quality of flax and potato.

Liming enriches the soil with calcium and, in many cases (e.g. when dolomitic meal is used), magnesium.

In most soils, calcium and magnesium are present in amounts quite sufficient for nutrition of even the most demanding crops (Table 4.4).

Table 4.4. Content of Calcium and Magnesium in Various Soils (%)

Nutrient	Soils			
	soddy podsolic	grey forest	chernozems	sierozems
Ca	0.73	0.90	1.44	6.04
Mg	0.50	0.70	0.90	1.45

The total calcium content in all soils is much higher than that of magnesium. Most of calcium and magnesium are in the form of sparingly soluble inorganic compounds, such as carbonates, sulphates, phosphates, silicate and aluminosilicate minerals. Besides, they are present in the soil in an exchangeable form and (insignificant amounts) in the form of water-soluble salts (nitrates, chlorides, and bicarbonates) resulting from displacement of exchangeable calcium and magnesium into the solution and from gradual disintegration of silicate and aluminosilicate minerals and dissolution of carbonates. Exchangeable forms provide the principal source of calcium and magnesium for plant nutrition.

Exchangeable magnesium is usually present in soils in amounts four to six times as low as those of calcium. The content of exchangeable calcium and magnesium is especially high in sierozems and chernozems and decreases appreciably in grey forest and soddy podsolic soils. The lowest content of exchangeable calcium and, especially, magnesium is in light acid soddy podsolic soils (sandy and sandy loam). Moreover, in these soils, plant roots receive less calcium and magnesium cations because of the antagonism of hydrogen ions. Liming of such soils may be particularly important for crops assimilating large amounts of calcium and magnesium.

4.1.3 The Role of Calcium and Magnesium in Plant Nutrition

Calcium is necessary for normal growth of above-ground organs and roots of plants. The need in this nutrient becomes manifest as early as the sprouting stage. If calcium is deficient with a heavy predominance of univalent cations (H^+, Na^+, K^+) or Mg^{2+} cations in the nutrient solution, the physiological balance of the solution is upset, and the root system of plants is the first to suffer. The growth and development of roots are inhibited, they become thickened, do not form lateral rootlets and hairs, turn slimy, and darken. The surface root cells in direct contact with such a solution degrade, their walls become slimy because the pectinic substances and lipids impregnating them are dissolved in the absence of calcium, the cell contents escape, and the tissue turns to a slimy amorphous mass. As a consequence, the uptake of nutrients is upset.

Addition of calcium restores the physical balance of the nutrient solution. Calcium cations act as strong antagonists with respect to other cations (H^+, Na^+, K^+, Mg^{2+}, Al^{3+}, etc.) and prevent their excessive influx into the plant.

Calcium is also required for normal development of above-ground organs which become stunted if this nutrient is deficient.

The role of calcium in plants seems to be closely associated with photosynthesis. Although calcium does not constitute part of chlorophyll, green plants are always richer in this element. Fungi, for example, may grow well without calcium. The internal colourless leaves of cabbage are much poorer in it than the external chlorophyll-containing ones:

Cabbage leaves	Ca content (mg/100 g fw)
external dark green	1058
third from outside	216
internal yellow-green	71
the youngest yellow-white	32

Calcium deficiency stunts the growth of leaves, light yellow spots appear on them (chlorosis), then the leaves die away, while the older ones remain normal. Older leaves contain more calcium than younger ones, but it cannot be reutilized in plants. As leaves senesce, their calcium content increases.

Calcium intensifies metabolism in plants, plays an important role in carbohydrate transport, catalyzes the conversion of nitrogenous substances, and speeds up the dissociation of reserve proteins in germinating seeds. In addition, calcium is essential for formation of normal cell envelopes and establishment of a favourable acid-base equilibrium in plants.

Calcium is present in plants as pectinates, sulphates, carbonates, phosphates, and oxalates. A significant part of it (20-65%) is water-soluble, the rest being extractable from plants by treatment with weak acetic and hydrochloric acids.

Plants take up calcium throughout their active growth period. When nitrate nitrogen is present in the solution, calcium uptake is intensified, the opposite being true in the presence of ammonia nitrogen, due to the antagonism between Ca^{2+} and NH_4^+ cations. The uptake of calcium is prevented by hydrogen ions and other cations if their concentration in the solution is high.

Plants differ widely in calcium uptake. At high yields (20 to 30 centners of grain crops, 200 to 300 centners of root and tuber crops, and 500 to 700 centners of cabbage), crops take up the following amounts of this element (in kg CaO per hectare): rye, wheat, barley, and oat—20 to 40; pea, vetch, kidney bean, buckwheat, and flax—40 to 60; potato, lupine, maize, and sugar beet—60 to 120; clover, alfalfa, sunflower, hemp, and tobacco—120 to 250; cabbage—300 to 500. The most calcium-demanding crops are cabbage, alfalfa, and clover. They are also characterized by extremely high sensitivity to increased soil acidity.

However, calcium requirements of plants and their response to soil acidity do not always coincide. For example, all grain crops take up relatively small amounts of calcium but differ widely in their sensitivity to acidic reaction; rye and oat are tolerant to soil acidity, while barley and wheat are not. Potatoes and lupine are indifferent to high acidity but demand a lot of calcium.

As opposed to magnesium, calcium contents are low in seeds and much higher in leaves and stalks. This is why most of the calcium taken up from the soil is not withdrawn from circulation but finds its way into manure, via fodder and litter, and then returns to the soil.

Loss of calcium from the soil is due not so much to its removal during harvesting as to leaching.

Depending on the amount of precipitation, soil texture, vegetation cover, rates and forms of lime and inorganic fertilizers, calcium losses by way of leaching from the arable and subsurface soil layers may range from tens to 400-500 kg per hectare, in terms of CaO. Application of physiologically acidic inorganic fertilizers at high rates substantially increases the loss of this nutrient.

In the case of cultivation of cabbage, alfalfa, and clover on calcium-poor acid sandy and sandy loam soils, calcium may be required not only to neutralize soil acidity, but also to improve plant nutrition with this element.

Magnesium forms part of the chlorophyll molecule and is directly involved in photosynthesis. Yet chlorophyll contains but a minor portion of this element, about 10 per cent of its overall content in plant tissues. Magnesium is also a constituent of pectinic substances and phytin, which is accumulated primarily in seeds.

When magnesium is deficient, the chlorophyll content in the green parts of a plant decreases; leaves, especially the lower ones, become mottled (affected by calico) and discoloured between veins, the green colour persisting only along the veins (partial chlorosis). Then, the leaves gradually turn yellow, curl from the edges, and are shed prematurely. The development of plants is slowed down and their growth stunted.

Magnesium together with phosphorus is localized mainly in the growing parts and seeds of plants. Unlike calcium, it is more mobile and may be reutilized in plants. It migrates from older to younger leaves and, after flowering, is translocated from leaves into seeds where it is concentrated in the germ. There is more magnesium in seeds and less in leaves, as compared to calcium. Magnesium deficiency affects the yield of seeds, roots, and tubers to a greater extent than that of straw or haulm. This element plays a major role in various vital processes: it is involved in phosphorus transport in plants, activates certain enzymes (e.g. phosphatases), speeds up carbohydrate synthesis, and affects the oxidation-reduction processes in plant tissues. Adequate supply of magnesium to plants intensifies the

reduction processes in them and is conducive to accumulation of larger amounts of reduced organic compounds, such as essential oils, fats, and so on. Magnesium deficiency, conversely, initiates oxidative processes, the activity of peroxidase increases, while the contents of invert sugar and ascorbic acid decrease.

Magnesium requirements vary from one plant to another. At high yields, they take up anywhere from 10 to 80 mg MgO per hectare. The most magnesium-demanding plants are potato, sugar and fodder beets, tobacco, pulses, and leguminous grasses.

Plants sensitive to magnesium deficiency include hemp, millet, and maize.

Soils contain less magnesium than calcium. It is especially scarce in highly podsolized acid soils of light texture. Placing of magnesium-containing lime fertilizers into such soils raises crop yields considerably.

Thus, liming of acid soils improves the nutrition of plants with nitrogen and ash elements, i.e. phosphorus, calcium, magnesium, and molybdenum. Improved nutrition on limed soils can also be attributed to the fact that plants develop stronger roots and are capable of taking up more nutrients from the soil and fertilizers.

4.1.4 Effectiveness of Liming

Most crops respond positively to liming of acid soils by an appreciable increase in yield.

According to the results of field experiments in various parts of the USSR, calculated lime rates (reducing acidity to a weakly acidic reaction) on soils with different degrees of acidity give the following average yield increments during the first year (in centners per hectare):

spring wheat, barley, rye, oat	2-5
winter wheat	3-6
table beet and table cabbage	30-80
fodder beet and fodder cabbage	30-100
potato	5-20
clover (hay)	16-30
hemp (straw)	4-10
hemp (seeds)	1.5-2.5

The effectiveness of liming depends on soil acidity, cultivated crops, rates and forms of applied lime fertilizers. The higher the soil acidity and the lime rate, the greater the effectiveness of liming (Table 4.5).

Table 4.5. Average Increments of Crop Yields due to Liming (centners per hectare) on Soddy Podsolic Soils of Different Degrees of Acidity (according to Shilnikov)

Crop	Soil acidity								
	high			moderate			weak		
	$CaCO_3$ rate (t/ha)								
	2-4	4-6	6-8	2-4	4-6	6-8	2-4	4-6	6-8
Winter wheat	3.9	4.6	5.4	2.7	4.0	4.6	1.0	1.5	2.0
Winter rye	2.0	3.0	3.4	1.7	2.0	2.4	0.5	1.0	1.2
Barley	3.6	4.0	4.5	3.0	3.6	4.1	1.4	1.8	2.0
Oat	2.0	2.3	2.6	1.7	2.0	2.2	0.5	1.0	1.2
Spring wheat	2.0	2.4	2.6	1.0	1.5	2.0	0.5	0.8	0.8
Maize (for silage)	40	60	70	20	30	40	10	15	20
Perennial grasses (hay)	18	25	27	12	15	18	9	12	13
Sugar beet	35	60	80	30	40	60	—	40	40
	(at pH $\geqslant$ 5.6 chernozem)								
Potato	10	14	18	13	17	17	5	5	5

Crop yields increase more markedly when subjected to liming are highly acidic rather than moderately and weakly acidic soils, while on soils with the same acidity yield increments increase with lime rates from 2-4 to 6-8 tons per hectare.

Liming also improves the quality of crops, especially when magnesium-containing lime fertilizers are applied simultaneously with boron ones. Liming increases the content of sugars in root crops, protein and fat in seeds, carotene and ascorbic acid in grasses and root crops. Liming of acid soils improves the sowing properties of seeds which tend to give higher yields.

The changes induced in the soil by liming persist over a long period of time, therefore, the effect of liming at full rates continues for two cycles of seven- to eight-course rotation. Every ton of lime fertilizer accounts, on moderately to highly acidic soils, for an overall increment of the yield

of all crops in seven-course rotation equal to 6 to 8 centners of grain per hectare per cycle and 12 to 15 centners per hectare per two cycles.

The higher the lime rate, the longer the effect and the greater the effectiveness of liming (Table 4.6).

Table 4.6. Average Increments of Yields (%) of Oat, Clover, and Winter Rye due to Liming per Cycle of Four-Course Rotation

$CaCO_3$ rate (t/ha)	Rotation cycle			
	1st	2nd	3rd	4th
2.25 (0.3 of hydrolytic acidity)	6	8	0	0
4.50 (0.6 of hydrolytic acidity)	4	19	9	22
9.00 (1.2 of hydrolytic acidity)	10	25	23	30

Lime fertilizers are poorly soluble, their interaction with the soil is slow, it takes time for the favourable soil reaction to be established, and, therefore, the effect of liming becomes more pronounced in the course of time. The full effect is observed only on the second or third year after application of lime.

Liming is a prerequisite for effective application of fertilizers to acid soddy podsolic soils. Fertilizers on unlimed acid soils often do not lead to increased yields, especially of crops sensitive to acidity, such as wheat, beet, maize, clover, pulses, and vegetables. In other words, liming dramatically enhances the effectiveness of organic and inorganic fertilizers.

Joint application of lime and manure to acid soils ensures high and stable yields of farm crops. Lime accelerates the decomposition of manure and intensifies the uptake of the constituent nutrients by plants, while manure amplifies the positive effect of lime on soil properties. Liming in combination with manuring permits the manure rate to be cut in half without detriment to effectiveness and, at the same time, twice as large an area to be fertilized with manure.

Talking about inorganic fertilizers, their effectiveness on limed highly acidic soils, as compared to unlimed ones, increases two-fold on the average in the case of winter wheat,

rye, and barley and three- to five-fold in the case of clover.

An increase in yield due to lime and inorganic fertilizers applied jointly is much greater than the sum of increments due to their separate application. Liming accounts for a particularly high effectiveness of physiologically acidic ammonia and potassium fertilizers. When systematically applied to acid soddy podsolic soils with poor buffering properties, these fertilizers render the soils even more acidic. Therefore, when such fertilizers are applied to unlimed soil, yield increments gradually decrease, and in subsequent years the yield may be even lower than on the control plot as a result of heavy acidification of the soil.

The positive effect of lime on the effectiveness of physiologically acidic forms of inorganic fertilizers is more pronounced when they are applied to crops sensitive to high acidity (beet, maize, wheat, rye, clover, etc.).

The liming of acid soils not only increases crop yields, but also provides for substantial economic benefits. The high economic effectiveness of liming has been demonstrated by a stationary field experiment at the Central Experimental Station of the USSR Research Institute of Fertilizers and Agronomical Soil Science (Barybino, Moscow Region), started in 1940 and involving seven-course rotation. Lime was applied once (in 1940) at rates of 7 and 3.5 tons per hectare, then, each year, inorganic fertilizers were applied during two rotation cycles: 1 to 1.5 centners per hectare of ammonium nitrate, 2 to 3 centners of superphosphate, and 1 centner of potassium chloride (Table 4.7).

The expenditures involved in liming were returned by yield increments of the first year or two. Over two rotation cycles, the net return on liming was 486 rubles per hectare at full rate and 300.9 rubles at half rate, that is, the return on the expenditures involved was 12- to 15-fold.

The economic benefits derived from liming with crop rotation vary widely depending on the crop composition (Table 4.8).

The highest net and gross returns stem from vegetable crop rotation including crops extremely sensitive to liming of acid soils.

The results of numerous field experiments suggest that on highly and moderately acidic soils the expenditures

Table 4.7. Economic Benefits Offered by Liming

Indicator	Lime rate (t/ha)	
	7	3.5
Increase in the yield of all rotating crops due to liming (centners of grain per hectare):		
during the 1st rotation cycle	34.0	24.1
during the 2nd rotation cycle	53.8	29.4
over two rotation cycles	87.8	53.5
Expenditures involved in liming (cost of lime, its transportation and application) (rubles per hectare)	41.0	20.5
Return on liming (rubles per hectare):		
gross return over two rotation cycles on the entire amount applied	527.0	321.4
net return over two rotation cycles on the entire amount applied	486.0	300.9
net return over a year on the entire amount applied	37.4	23.1

Table 4.8. Net Return on Liming with Various Crop Rotations (according to Kornilov)

Crop rotations	Soil acidity	Lime rate (t/ha)	Return (rubles/ha)
Eight-course field crop rotation	High and moderate	3.0	254
	Low	2.0	88
Six-course near-farm fodder crop rotation	High and moderate	4.0	349
	Low	3.0	156
Seven-course vegetable crop rotation	High and moderate	4.0	971
	Low	3.0	415

involved in liming are paid back by the crop return over a period of 1.3 years in the case of grain crops, within less than a year in the case of fodder crops, and within a year, three- to five-fold, in the case of potatoes and vegetables. On weakly acidic soils, the return period increases 1.5-fold.

Over a rotation cycle, the return on liming is 12- to 13-fold.

4.1.5 Lime Fertilizers

Lime materials are derived by crushing or calcining hard calcareous rocks (limestone, dolomite, or chalk). Another group of materials used for liming includes soft calcareous minerals, which do not require crushing, and industrial waste rich in lime.

Hard Calcareous Rocks

Hard calcareous rocks contain primarily $CaCO_3$ and $MgCO_3$ plus an insoluble residue (clay and sand). Depending on the CaO and MgO contents, these rocks are divided into the following groups (according to Vishnyakov): *limestones* containing 55-56% CaO and up to 0.9% MgO; *dolomitic limestones* containing 42-55% CaO and 0.9-9% MgO; and *dolomites* containing 30-32% CaO and 18-20% MgO.

As far as the contents of clay, sand, and other admixtures are concerned, hard calcareous rocks are divided into the following groups: *pure calcareous rock* (limestone, dolomite) containing not more than 5 per cent of admixtures; *marlaceous* or *arenaceous calcareous rock* containing 5 to 25 per cent of admixtures, and *marl* or *silty calcareous rock* containing 25 to 50 per cent of clay or sand.

Large amounts of admixtures lower the quality of calcareous rocks. When they are present in amounts exceeding 15 to 20 per cent, the use of such rocks as fertilizers is justified only if purer materials are not available.

Limestones and chalk are sedimentary rocks of sea origin, as a rule.

Limestones contain primarily calcite ($CaCO_3$), although they are often dolomitized and also contain $MgCO_3$ (up to 10-15% MgO). The presence of $MgCO_3$ accounts for hardness of calcareous rocks and makes them less soluble. Depending on the composition and content of the admixtures (organic substances, iron and manganese compounds) limestones may be white, greyish, yellowish, or brown. Chalk contains up to 55% CaO and a small amount (0.02-0.6%) of MgO; it differs from limestones by being softer and more friable. It is faster in action than crushed limestone, which makes it a more effective fertilizer, especially within the first year after application.

Dolomites consist of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$). Pure dolomite contains 54.4% $CaCO_3$ and 45.6% $MgCO_3$. Dolomites and dolomitic limestones are harder and more difficult to crush than chalk and limestone. At the same time, they are less readily soluble ($MgCO_3$ is virtually insoluble in water and sparingly soluble in water containing carbon dioxide). Hard calcareous rocks serve as a source of lime fertilizers, such as crushed limestone, dolomitic meal, burnt and slaked lime.

Crushed limestone and dolomitic meal are produced by crushing and grinding limestones and dolomites. The speed of interaction with the soil and effectiveness of these materials as fertilizers are strongly dependent on the particle size. Limestone and dolomite particles larger than 1 mm are poorly soluble and reduce soil acidity but insignificantly. For example, in an experiment conducted at the department of agricultural chemistry of the Timiryazev Agricultural Academy in Moscow, after application of lime with a particle size of 1 mm to an acid soil (pH 4.5), the neutralization of soil acidity after ten months was slight (to pH 4.7), while application of lime with a particle size of 0.1 mm had led to a considerable reduction in acidity (up to pH 5.8).

The smaller the particle size of crushed limestone or dolomitic meal, the more readily it is mixed with the soil, the faster and more complete its dissolution, the more rapid and effective its action (Table 4.9).

Table 4.9. Barley and Vetch Yield Increments (% of the check yield) (averaged over two years)

Experiments	$CaCO_3$ rate (t/ha)	$Ca(OH)_2$*	Limestone		
			coarse (2-1 mm)	medium (1-0.25 mm)	fine (less than 0.25 mm)
Field (results averaged over four plots)	3	32	4	12	20
	9	33	3	7	19
Greenhouse (results averaged over four soils)	3	60	11	18	40
	9	66	15	30	51

* $Ca(OH)_2$ was applied at rates of 2.25 and 6.25 tons per hectare.

The results of field experiments carried out at the USSR Research Institute of Fertilizers and Agronomical Soil Science, as well as the Lithuanian and Latvian Research Institute of Agriculture indicate that the most effective material is pulverized limestone with a particle size of 0.25 mm. An increase in yield due to application of material with a particle size of 1.0 to 0.25 mm was about 20 per cent lower, while in the case of particle sizes ranging from 1 to 3 mm it was almost twice as low.

Lime particles larger than 3 mm are not as effective.

The optimal particle size is considered to be 0.2 to 0.3 mm because finer particles do not increase the effectiveness of limestone.

The importance of particle size increases with the hardness of limestones. Therefore, more stringent requirements are imposed on the particle size of dolomites.

At high contents of coarse particles (larger than 1 mm), the effectiveness of crushed limestone and especially dolomitic meal perceptibly decreases. At the same time, if they contain too much of the extremely fine fraction (less than 0.25 mm), these materials tend to become dusty, and mechanization of their application is difficult.

At present, two grades of crushed limestone are produced in this country: pulverized and ground. They should meet the following requirements of the appropriate state standard (GOST): *pulverized* material must pass in its entirety through a sieve with mesh size 3.0 mm, 95 per cent should pass through a sieve with mesh size 1.0 mm, and at least 70 per cent through a sieve with mesh size 0,25 mm, the impurities constituting not more than 15 per cent and the moisture content not exceeding 1.5 per cent; *ground* limestone must be retained in an amount of 8 per cent on a sieve with mesh size 5 mm, 30 per cent on a sieve with mesh size 1 mm, and 55 per cent on a sieve with mesh size 0.25 mm, the moisture content not exceeding 15 per cent.

If the moisture content is too high, crushed limestone does not flow as easily and becomes difficult to sift, and in winter it tends to freeze into lumps. Finely pulverized limestone must be stored dry under a shed or in large heaps covered with straw or peat. Broadcasters are used for its application.

Burnt and Slaked Lime. When hard limestones are calcined, calcium and magnesium carbonates lose carbon dioxide and turn to calcium or magnesium oxide, yielding burnt lime (or quicklime):

$$CaCO_3 = CaO + CO_2$$
$$MgCO_3 = MgO + CO_2$$

Its interaction with water leads to formation of calcium or magnesium hydroxide, which is known as slaked lime, in the form of a fine powder:

$$CaO + H_2O = Ca(OH)_2$$
$$MgO + H_2O = Mg(OH)_2$$

Burnt lime can be slaked directly in the field by burying it under moist earth.

Slaked lime comes as waste in the production of lime and bleaching powder. In this case, it may contain many lumps that have to be screened off.

In its capacity to neutralize soil acidity, one ton of $Ca(OH)_2$ is equivalent to 1.35 tons of $CaCO_3$.

Powder lime is a quick-acting fertilizer especially recommended for clayey soils. It is much more readily soluble in water (by about a factor of 100) than lime carbonate (however, magnesium hydroxide is almost insoluble in water).

Experiments carried out at the USSR Research Institute of Fertilizers and Agronomical Soil Science and other research centres indicate that within the first year after application slaked lime is more effective than lime carbonate. During the second year, the difference becomes less pronounced, and in subsequent years their effectiveness is equalized. Slaked lime is more expensive than $CaCO_3$, and its action is less prolonged because of the more rapid leaching of calcium.

Soft Calcareous Minerals

Deposits of soft calcareous minerals can be found almost in every region and republic of the Non-Black Earth zone of the USSR.

In contrast to hard rocks, these minerals are secondary freshwater lime deposits. They do not require crushing, are more effective, and act more quickly than crushed limestone.

Numerous local deposits of soft calcareous minerals occur near fields that require liming, which allows it to be performed using these cheap local materials at lower expenditures of labour and money.

Calc-tufas (spring lime) contain 90-98% (sometimes 80-90%) $CaCO_3$; less frequent are tufas containing not more than 70% $CaCO_3$ and larger amounts of mineral and organic admixtures. Their deposits are most common in erosional flood plains at spring openings.

Calc-tufas represent a loose, porous, readily crumbling grey mass, sometimes tinted with dark, brown, and rusty hues due to admixtures of ferric hydrate and organic matter. Tufas often contain a certain amount of coarser and harder particles that must be screened off or crushed prior to application.

Gaja (lake lime) contains 80-95% $CaCO_3$, its deposits being associated with dried up lakes formerly receiving calcium-rich water. Lake lime has a fine-grained texture, crumbles readily, and is easy to crush, primarily into particles less than 0.25 mm in size, which makes it an effective lime fertilizer.

Marl contains 25-50% $CaCO_3$, some $MgCO_3$ and other admixtures. It is a mineral in which calcium carbonate is mixed with clay and often with clay and sand. Marl occurs in nature as a friable mass or compact rock. Compact marl must be carried to the field in winter and piled up in small mounds. Under the effect of moisture and temperature changes it becomes loose, crumbles into small particles, and can be easily incorporated into the soil. The marl rate is selected depending on its $CaCO_3$ content. When applied in amounts equivalent to crushed limestone in terms of $CaCO_3$, marl is as effective as the latter.

Peaty tuff is a lowland mineral rich in lime. It contains 10-70% $CaCO_3$. This valuable peat-lime fertilizer is recommended for liming of acid soils deficient in organic matter and located near peaty tuff deposits.

Natural dolomitic meal contains both $CaCO_3$ and $MgCO_3$ (a total of 95 per cent and above in terms of $CaCO_3$). It occurs near calcareous deposits at depths ranging from 40 to 80 cm in a layer 1-2 m thick, and even thicker, or intercalations within hard dolomites.

Dolomitic meal is a loose mass of fine texture with 98 per cent of particles smaller than 0.25 mm, sometimes interspersed with pieces of hard rock, which must be screened off before application. This is a highly valuable lime fertilizer because in addition to calcium it also contains magnesium.

In experiments carried out at the USSR Research Institute of Fertilizers and Agronomical Soil Science and other research institutions, magnesium-containing lime fertilizers (ground dolomite, dolomitic limestones, natural dolomitic meal, etc.) were found to be more effective on highly acidic soils with a low degree of base saturation than magnesium-free lime materials. They are especially advantageous on sandy and sandy loam soils deficient in this nutrient (Table 4.10).

Table 4.10. Comparative Effect of Dolomitic Meal and Lime Carbonate on Crop Yields (according to the USSR Research Institute of Fertilizers and Agronomical Soil Science)

Crop	Number of samplings	Average yield increment (centner/ha) due to	
		dolomitic meal	lime carbonate
Sandy and Sandy Loam			
Winter rye	1	5.1	4.4
1st and 2nd year clover (hay)	4	33.3	26.2
Flax (straw)	1	15.6	3.5
Flax (seeds)	1	2.1	0.8
Potato	2	155.2	37.7
Moderately Heavy and Heavy Loam			
Clover with timothy	8	22.7	23.9
Winter wheat	2	3.4	3.3
Potato	3	8.4	3.3

Gedroits and Kedrov-Zikhman have established that the positive effect of liming on most farm crops is complete only if calcium and magnesium are present in the soil solution and absorbing complex in a ratio favourable for their growth and development. Plants may develop at various ratios between

these cations, but the optimal conditions for most plants are created when the soil contains 40 to 80 parts of Mg for every 100 parts of Ca.

Highly acidic soddy podsolic soils with a low degree of base saturation and light texture often contain less exchangeable magnesium than is required to maintain the optimal ratio with calcium. When lime fertilizers containing only $CaCO_3$ are applied, the unfavourable ratio between the two nutrients gets worse. An extremely high calcium-to-magnesium ratio in the absorbing complex and soil solution is responsible for the low effectiveness and even harmful effect of lime on some plants.

Application of lime materials containing calcium with a sizable amount of magnesium improves the ratio between these nutrients in the absorbing complex and soil solution, which is why the yields of some crops increase more significantly than in the case of lime fertilizers containing no magnesium.

Particularly sensitive to application of magnesium-containing lime fertilizers are sugar, table and fodder beets, root crops (carrot, rutabaga, etc.), clover, alfalfa, flax, potato, maize, barley, buckwheat, onion, and oil-bearing plants. $MgCO_3$ in lime fertilizers neutralizes the negative effect of liming on flax, potato, lupine, and seradella, which do not tolerate high amounts of calcium carbonate. Less sensitive to lime materials containing magnesium are most grain crops (wheat, rye, oat), cereal grasses, cabbage, and lettuce.

Industrial Lime Waste

Other materials suitable for liming include lime cakes, shale ash, various metallurgical slags, lime production waste, and other industrial waste rich in lime. Their effectiveness is as high as that of crushed limestone, and their use is even more economical because no expenditures associated with lime quarrying and crushing are involved.

Shale ash results from burning of combustible shales at industrial enterprises and electric power plants. It contains 30-48% CaO and 1.5-3.8% MgO and has a high neutralization capacity. In addition, shale ash contains potassium, sodium, sulphur, phosphorus, and some micronutrients,

which makes it an extremely effective fertilizer. Most of calcium and magnesium are present in it in the form of silicates less readily soluble than carbonates, which is why it reduces soil acidity somewhat less vigorously and more slowly as compared to calcium carbonate. This, however, does not detract from its value, and for some crops (flax, potato, etc.) this property is beneficial. Even when applied at high rates (up to 20 t/ha), shale ash enhances the yield of such crops. Its advantage over calcium carbonate in the case of potatoes is illustrated by the following data (Table 4.11).

Table 4.11. Effect of Shale Ash and Gaja on Potato Yields (according to the USSR Research Institute of Fertilizers and Agronomical Soil Science)

Experimental conditions	Yield (cent/ha)	
	without fertilizers	NPK
Without liming	96.2	167.7
Shale ash	114.0	162.8
Gaja	83.2	172.8

The shale ash coming from large industrial enterprises where shales are crushed before being burnt has an extremely fine texture. According to Kornilov, it may contain 92 per cent of particles smaller than 1 mm, of which 56 per cent are particles smaller than 0.16 mm. Such an ash, however, produces a lot of dust when dry, while humidity causes it to form hard lumps. Therefore, it should not be stored outdoors unprotected, transported in open vehicles, and applied by conventional broadcasters. Shale ash is normally transported and applied by means of cement trucks or broadcasters with special attachments. The moisture content in it should not be less than 5 and more than 15 per cent.

Burning of uncrushed shale yields coarse ash with predominance of large particles. Such ash must be sifted or ground before application. Each year, about 3 million tons of shale ash are used.

Lime cakes are essentially beet-sugar production waste. They contain mainly $CaCO_3$ with admixtures of $Ca(OH)_2$

and a small amount of N, P_2O_5, K_2O, and organic matter. The fresh waste (lime sludge) contains about 40% water. After drying in air, its water content goes down to 25-30%, it becomes loose and can be used as fertilizer. Dry lime cakes contain 60-75% $CaCO_3$, 10-15% organic matter, 0.2-0.7% N, 0.2-0.9% P_2O_5, and 0.3-1.0% K_2O. They can be used for liming acid soddy podsolic and grey forest soils and also as a local fertilizer on podsolized and leached chernozems in regions of sugar beet cultivation. Lime cakes are effective on soils with a hydrolytic acidity of at least 2 meq/100 g. Experiments run by Ukrainian research institutes and collective farms have shown that application of 3 to 5 tons of lime cakes per hectare with deep ploughing beginning in autumn raises sugar beet yields on acid soils by 30 to 55 centners per hectare.

According to the USSR Research Institute of Fertilizers and Agronomical Soil Science, lime cakes are more effective than lime carbonate in terms of CaO. More than 3 million tons of lime cakes are used annually.

Blast-furnace and open-hearth slags are waste materials of cast iron and steel production and have different compositions: 30-50% CaO, 12-37% SiO_2, 10-15% Al_2O_3, 2-10% MgO, 0.4-5.6% MnO, 0.1-3.5% P_2O_5, and 0.1-4.5% R. In most cases, they require preliminary crushing and grinding. Most of calcium in slags is present in the form of less readily soluble silicates ($CaSiO_3$ and Ca_2SiO_4), therefore, they must be ground to a smaller particle size than crushed limestone. Basic slags (containing more than 40% CaO + MgO) approach lime carbonate in neutralization capacity. They are often more effective than lime because they contain magnesium, phosphorus, manganese, sulphur, and other nutrients. Moreover, the silicic acid present in them may reduce the content of mobile aluminium in soils and facilitate the uptake of phosphorus by plants. Metallurgical slags rich in lime are valuable fertilizers for soddy podsolic soils in the neighbourhood of iron and steel works.

White lime slag is a waste product of electric steel smelting in the form of a white fine powder suitable for liming without preliminary grinding. It contains 50-68% CaO, 6-15% MgO, 15-25% SiO_2, as well as phosphorus, manganese, sulphur, and other nutrients. Calcium is present in the

slag as CaO, which is more active than $CaCO_3$. In terms of neutralization capacity, one ton of the slag is equivalent to 1.2-1.4 tons of crushed limestone. When applied in advance (1.5 to 2 weeks before sowing), it is more effective than lime carbonate and at least as effective as powder lime.

Dolomitic dust is metallurgical waste resulting from burning of dolomite in cupolas. Fresh dolomitic dust consists primarily of CaO and MgO which gradually turn to $CaCO_3$ and $MgCO_3$ on storage. In terms of neutralization capacity, one ton of dolomitic dust is equivalent to 1.5 tons of $CaCO_3$. Dolomitic dust naturally needs no grinding, but, when applied from a broadcaster, coarse particles must be screened off. Its effect on the yield of legumes, root crops, flax, and potatoes is more tangible than that of lime fertilizers containing only calcium.

Belitic meal is a waste product of aluminium production (sludge), containing 45-50% CaO, 25% $Na_2O + K_2O$, up to 30% SiO_2, 2.9% Fe_2O_3, 0.04% MnO, 3.4% Al_2O_3, and small amounts of phosphorus, sulphur, and some micronutrients. It has a good texture with 95 per cent of particles less than 1 mm in size, including about 50 per cent of particles smaller than 0.15 mm. Its effectiveness is as high as that of any other lime fertilizer.

Lime fertilizers also include leather, soda, gas, cement, and soap production waste, waste from pulp-and-paper mills, and other industrial waste in which calcium and magnesium are present in the form of oxides, hydroxides, carbonates, and silicates without any admixtures harmful to plants.

4.1.6 Desirability of Liming

Whether liming is desirable or not can be estimated from certain manifestations. Highly acidic soils are whitish and have a prominent podsolic layer ten and more centimetres thick. There is no question that such soils must be limed.

High soil acidity and desirability of liming are also indicated by the status of certain cultivated crops and weed infestation. Stunted growth and pronounced spareness of clover, alfalfa, beet, winter wheat, and other crops sensitive to high acidity (in spite of adequate agricultural practices, application of appropriate fertilizers, and other favourable

conditions) are telltale signs that liming is called for. Some weeds and wild plants, such as sheep sorrel, spurrey, hemp nettle, creeping buttercup, matgrass, hair grass, rush, ledum, and heather, thrive on acid soils. Their abundance on fields and meadows is indicative of high soil acidity and desirability of liming.

Whether plants require liming can be established more firmly by way of agrochemical analysis of the soil, determination of its exchange acidity (pH of the salt extract), and degree of base saturation (V). Depending on the exchange acidity of a soil with an average humus content of 2 to 3 per cent, the desirability of liming is classified as follows: high desirability corresponds to pH 4.5 and below, moderate, to pH 4.6-5.0, low, to pH 5.1-5.5, and no need in liming at pH 5.5 and above. The pH value of the salt extract indicates precisely, on the one hand, soils that need liming badly and will be radically improved by it and, on the other, soils that do not have to be limed at all and will not respond to liming. It is difficult to differentiate between soils of intermediate acidities (pH 4.5-5.5) on the strength of pH alone.

The degree of soil acidity is an important but not the only indicator of desirability of liming. Other factors of importance include the content of mobile aluminium and manganese compounds in the soil, the degree of its base saturation, and soil texture.

Depending on the degree of base saturation, soils fall under the following categories: $V = 50\%$ and below, liming is highly desirable; 50-70%, the desirability of liming is moderate; 70% and above, liming is less desirable; above 80%, the soil needs no liming. At equal pH values, soils with a higher degree of base saturation need liming to a lesser extent. The desirability of liming can be assessed more exactly by taking into account the pH value of the salt extract along with the degree of base saturation and soil texture (Table 4.12).

In this case, soil groups according to desirability of liming are more clearly defined and agree well with its effectiveness as established in field experiments.

Another factor to be taken into consideration in liming is characteristics of individual rotating crops. In the case of field crop rotation with a small percentage of flax and pota-

Table 4.12. Desirability of Liming Depending on Soil Properties (according to Kornilov)

Soils	Desirability of liming							
	high		moderate		low		none	
	pH	V	pH	V	pH	V	pH	V
Heavy and moderately loamy	< 5.0	< 45	5.0-5.5	45-60	5.5-6.0	60-70	> 6.0	> 70
Loamy	< 5.0							
Light loamy	< 4.5	< 50	4.5-5.0	50-65	5.0-5.5	65-75	> 5.5	> 75
Sandy loamy and sandy	< 4.0	< 55	4.0-4.5	55-70	4.5-5.0	70-80	> 5.0	> 80
Light loamy	< 5.0	< 35	5.0-5.5	35-55	5.5-6.0	55-65	> 6.0	> 65
	< 4.5	< 40	4.5-5.0	40-60	5.0-5.5	60-70	> 5.5	> 70
	< 4.0	< 45	4.0-4.5	45-55	4.5-5.0	65-75	> 5.0	> 75
Sandy loamy and sandy	< 5.0	< 30	5.0-5.5	30-45	5.5-6.0	45-55	> 6.0	> 55
	< 4.5	< 35	4.5-5.0	35-50	5.0-5.5	50-60	> 5.5	> 60
	< 4.0	< 40	4.0-4.5	40-55	4.5-5.0	55-65	> 5.0	> 65
Peat and peat-boggy	< 3.5	< 35	3.5-4.2	35-55	4.2-4.8	55-65	> 4.8	> 65

toes as well as crops sensitive to acidity (vegetables, fodder crops, etc.), the liming schedule is consistent with the classification of soils according to desirability of liming (Table 4.12): soils for which liming is highly desirable must be treated in the first place, those for which the desirability of liming is moderate must be treated next, and those whose liming is less desirable must be treated last (Table 4.13).

Table 4.13. Desirability of Liming Depending on Soil Properties and Rotating Crop Composition

Desirability of liming depending on soil properties (Table 4.12)	Liming schedule depending on rotating crop composition		
	small percentage of flax and potato, vegetable and fodder crops	high percentage of flax and potato	in vegetable and fodder crop rotations
High	First turn	First turn	First turn
Moderate	Second turn	Second turn	First turn
Low	Third turn	No liming	Second turn
None	No liming	No liming	Third turn

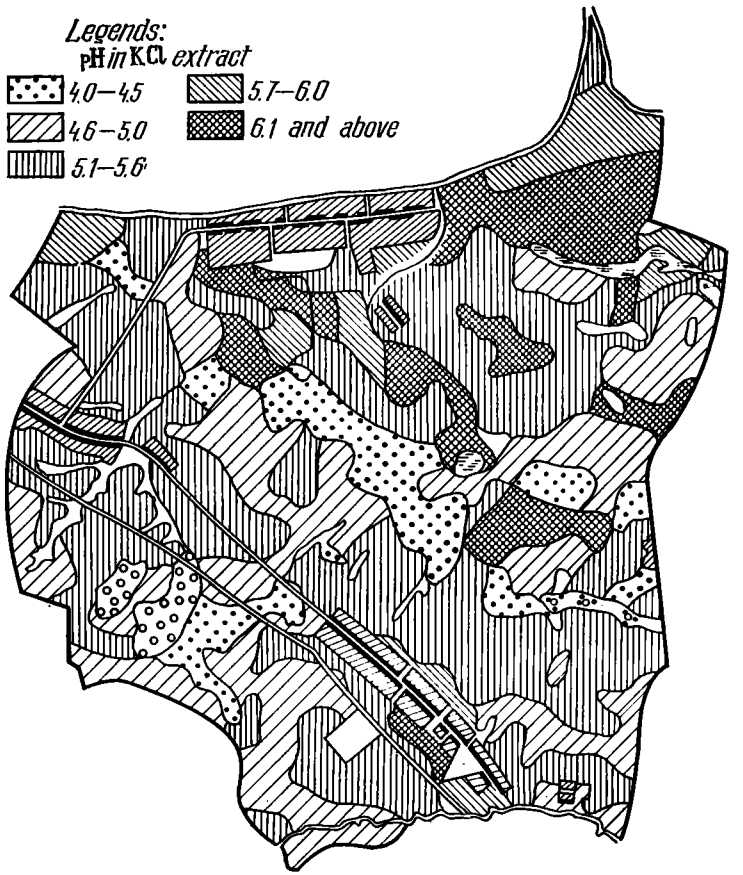


Fig. 4.2: Farm field soil acidity chart

With a different crop composition, the liming schedule according to soil groups will be somewhat different.

To better organize liming procedures, zonal agrochemical laboratories together with planning and surveying stations of chemicalization produce, from the results of agrochemical soil analysis, charts showing areas with different degrees of soil acidity and liming requirements (Fig.

4.2) and send them to farms. Since soil processes and applied fertilizers change the pH values of soils, the agrochemical analyses are periodically (every 4 to 5 years) repeated to update the previously prepared charts.

In compliance with the local conditions, i.e. areas covered by soils that need liming, availability of the necessary machinery, vehicles, lime fertilizers, and so on, each farm must have a long-range plan for liming procedures. TsINAO has developed a software package (ISKRA) to handle liming project estimates defining the areas to be limed from one year to another, specifying lime rates and overall lime fertilizer requirements, assigning vehicles and machinery for liming, and outlining the expenditures involved in liming and the expected return. Collective and state farms finance chemical amelioration activities from the state budget allocations.

4.1.7 Lime Fertilizer Rates

Prior to liming, it is extremely important to establish optimal lime rates depending on soil and crop properties. The quantity of lime, required to reduce the high acidity of the arable soil layer to a weakly acidic reaction (water extract pH 6.2-6.5, salt extract pH 5.6-5.8) favourable for most crops and useful microorganisms, is referred to as full rate. It depends on the degree of soil acidity.

The full rate of lime can be determined most accurately from hydrolytic acidity. To calculate the lime rate (in tons of $CaCO_3$ per hectare), the hydrolytic acidity (H_h) expressed in milliequivalents per 100 g of soil is multiplied by the coefficient 1.5: $CaCO_3$ rate $= H_h \times 1.5$. This formula has been derived from the following calculations. To neutralize 1 meq of acidity (H^+ ions) per 100 g of soil takes 1 meq or 50 mg $CaCO_3$, or in terms of 1 kg of soil, 500 mg $CaCO_3$; multiplication of this quantity by the weight of the arable layer over an area of one hectare (3 000 000 kg), followed by division of the product by 1 000 000 000 (to convert milligrams into tons), gives:

$$CaCO_3 \text{ rate} = \frac{H \times 500 \times 3\,000\,000}{1\,000\,000\,000} = H_h \times 1.5$$

Experiments have shown that the soil reaction can be reduced to a weakly acidic pH value by neutralizing two thirds of hydrolytic acidity. This is why lime is often applied at two thirds of the rate calculated from total hydrolytic acidity. The $CaCO_3$ rate is then numerically equal to hydrolytic acidity. If lime fertilizers containing $MgCO_3$ or CaO and $Ca(OH)_2$ rather than $CaCO_3$ are used in liming, the calculated lime rate is to be multiplied by 0.84 for $MgCO_3$, 0.74 for $Ca(OH)_2$, and 0.56 for CaO.

When lime materials contain sizable amounts of impurities and large particles (larger than 1 mm), the following correction formula is used:

$$\frac{\text{$CaCO_3$ rate found from soil acidity} \times 100 \times 100}{\text{\% $CaCO_3$ in fertilizer} \times (100 - \text{\% of particles larger than 1 mm})}$$

For example, the $CaCO_3$ rate determined from soil acidity is 4 t/ha; the soil is to be treated with a lime fertilizer containing 80% $CaCO_3$ (or all neutralizing substances in terms of pure $CaCO_3$) and 25% particles larger than 1 mm. Then, the lime rate in physical units is

$$\frac{4 \times 100 \times 100}{8(100-25)} = 6.6 \text{ t/ha}$$

Theoretically, the lime rate determined from hydrolytic acidity must bring the soil reaction up to pH 8.2. However, under actual field conditions, because of insufficient mixing and slow interaction of lime with the soil, the reaction is brought to weakly acidic or close to neutral (pH 5.5-6.5), which is favourable for most crops.

When the lime rate is established for a particular application, in addition to soil acidity the rotating crop characteristics and soil texture are taken into account. The full rat calculated from hydrolytic acidity is not optimal for all crops and soils.

A lime rate is considered optimal if it ensures stable and prolonged action on crop yields and provides for a good return. The optimal rate may correspond to hydrolytic acidity completely or partially. For rye, winter and spring wheat, barley, oat, maize, sugar, fodder and table beets, clover, alfalfa, pulses, cabbage, and onion grown on moderately and heavily loamy soddy podsolic soils, it corresponds

to the full rate calculated from hydrolytic acidity. On light soils with low buffering capacity, the lime rate should be reduced by 25 to 30 per cent of the full rate. The optimal rate for flax, sunflower, tomato, potato, lupine, and seradella, the reduction is to one half or two thirds of the full rate.

Lime rates can also be determined from the pH of the salt extract with due account for soil texture. The USSR Research Institute of Fertilizers and Agronomical Soil Science recommends the following lime rates for soddy podsolic soils containing a maximum of 3 per cent of organic matter (Table 4.14).

Table 4.14. Lime Rates as a Function of Soil pH and Texture

Soils	Salt extract pH					
	⩽4.5	4.6	4.8	5.0	5.2	5.2-5.4
	$CaCO_3$ rate (t/ha)					
Sandy loam and light loam	4.0	3.5	3.0	2.5	2.0	2.0
Moderately heavy and heavy loam	6.0	5.5	5.0	4.5	4.0	3.5

The determination of lime rates from soil pH and texture is based on the fact that the resistance of soils to changes in its reaction caused by liming is to some or other extent related to their texture: the heavier the soil, the more lime is needed to change its reaction. This method, however, has its drawbacks. The pH value is not a direct measure of acidity, hence, it cannot be used as a direct indicator of how much lime is needed to neutralize soil acidity. Moreover, the resistance of soils to changes in its reaction due to liming depends not only on the texture, but also on the mineralogical composition of the heavy fraction as well as on the content of organic matter in the soil. Therefore, lime rates determined from soil pH and texture do not ensure the necessary changes in reaction on all soils.

The lime rate necessary to optimize soil reaction can also be determined from the buffering capacity of the soil. In this case, added to weighed amounts of soil are increasing quantities of an alkali, and the resulting pH value is meas-

ured after establishment of a state of equilibrium. The results are plotted in the form of a titration curve which clearly shows how much lime is needed to achieve the desired soil pH. However, methods for determining the buffering capacity of soils are very time-consuming and do not lend themselves easily to routine use.

4.1.8 Liming Procedures

Full rates of lime are applied at once or in several steps. In the former case, the acidity of the entire arable layer is neutralized quickly and completely for a long period of time to ensure higher returns of most farm crops. Liming at full rate is particularly important in the cultivation of crops sensitive to acidity on highly acidic soils, as well as in deepening of the arable layer of inadequately cultivated soddy podsolic soils.

If a farm cannot treat at once the entire area of acid soils with lime at full rate, the latter can be halved to treat twice as large an area. In this case, the increase in yield per hectare will be 20 to 30 per cent lower (when inorganic fertilizers are applied at high rates, even about 50 per cent lower), yet, the overall increase over the entire area treated with lime will be greater within the first few years than after application at full rate but over an area half as small.

The first years after liming demonstrate that the difference in effectiveness between full and half rates is relatively small. During the second crop rotation cycle, yield increments due to liming at half rate become almost twice as small as compared to liming at full rate (Table 4.15).

Liming at full rate is effective, as far as the yield increase is concerned, for as long as 12 to 15 years on moderately heavy and heavy loams and 8 to 10 years on soils having a light texture. In the former case, treatment at full rate is repeated after two cycles of a seven-to-eight-course rotation, and in the latter, after one cycle.

The positive effect of liming at half rate is less durable. The second half of the full rate is therefore applied over the same area again after six to seven years. Systematic application of inorganic fertilizers, especially physiologically acidic ones, at high rates leads to markedly increased losses of

Table 4.15. Effectiveness of Various Lime Rates on an Acidic (pH_{KCl} 4.0) Heavily Loamy Soddy Podsolic Soil

Lime rate	Grain yield (cent/ha)			
	1st rotation cycle		2nd rotation cycle	
	overall	increase due to liming	overall	increase due to liming
Background (NPK)	84.4	—	154.0	—
Background + lime at full rate (7.2 t/ha)	115.6	31.2	205.9	51.9
Background + lime at half rate (3.6 t/ha)	106.5	22.1	180.7	26.7

calcium and magnesium, and the soils limed earlier soon become more acidic. In this case, liming should be repeated after a shorter period of time to ensure that each hectare receives at least five to six centners of lime, on the average, every year.

The periodicity and effectiveness of repeated liming depend on the lime rate during the first application and availability of inorganic fertilizers at the farm. In the case of liming at half rates and intensive application of inorganic fertilizers, lime is applied more often, and the effectiveness of repeated treatment with lime is rather high. The need to repeat liming is determined through agrochemical analysis of the soil (determination of its acidity) and calculation of the calcium balance from the results of lysimeter experiments.

Liming at full and half rates is performed during autumn ploughing or second ploughing in spring. Lower lime rates, that is, one quarter to one fifth of the full rate (0.5-1 t/ha), are not sufficient to reduce the acidity of the entire arable layer. Consequently, lime is placed in drill rows during sowing and in holes during transplantation of seedlings so as to minimize soil acidity in the root zone. Liming at low rates creates ideal conditions for growth and increases yields only of the crop for which it is intended. During the first reploughing, lime is mixed with the entire arable layer, its acidity remains virtually the same, and the effect of fertilizing on subsequent crops drops sharply or becomes nil.

Therefore, lime should be applied at low rates four to five times within a rotation cycle to crops sensitive to acidity. In this case, accomplishment of the main task of liming, that is, reduction of high soil acidity, is postponed indefinitely, and liming becomes more time-consuming.

Liming at low rates may be advisable only as an additional measure to enhance the yields of crops sensitive to acidity, such as clover, winter wheat, beet, maize, and others.

For example, plough-under liming at half rate in flax and potato rotation may be combined with local placing of lime in drill rows to fertilize crops highly sensitive to acidic reaction.

Lime is also used to neutralize the potential acidity of inorganic fertilizers. Liming to this end prevents further acidification of the soil and raises the effectiveness of the fertilizers. To neutralize the acidity of a centner of ammonium sulphate takes 1.3 centners of $CaCO_3$, one centner of lime being required to neutralize the acidity of a centner of ammonium nitrate and one tenth of that amount for a centner of superphosphate.

4.1.9 Use of Lime Fertilizers in Crop Rotation

The effectiveness of liming is strongly dependent on uniform application of lime fertilizers and their intimate mixing with the soil. The most even distribution of lime over the field surface is attained by means of lime broadcasters. Powdered lime fertilizers, cement kiln dust, and shale ash are handled by cement trucks or other vehicles of the same type. Lime is best mixed with the soil when applied to clean fallow or to row and vegetable crops during autumn ploughing. In this case, it is properly mixed with the entire arable layer during the subsequent tillage in spring or inter-row tillage in summer.

Liming in summer is more difficult because of the lack of vacant fields so that the time available for liming is restricted to April-May, before spring crops are sown, and to September-October, after their harvesting. This is why liming in winter has gained in popularity in recent years. In exceptional cases, lime can be spread over frozen ground, shallow or melting snow (in November, December, March,

and early April) with subsequent incorporation during spring ploughing. To avoid lime losses due to entrainment by winds from the snow cover and by streams of melt water from slopes, liming in winter must be carried out on levelled ground with a grade of not more than 5 degrees under no-wind or slack wind conditions (at a wind velocity not exceeding 4-5 m/s) with lime being incorporated into snow. It is important to use lime with a maximum moisture content of 8 per cent for use in winter (to avoid its freezing into lumps). Experience has shown that, if properly performed, liming in winter is as effective as during the usual periods of time. An additional benefit of liming in winter is that machinery is used more fully throughout the year.

In vegetable and fodder crop rotations, all types of lime fertilizers are involved; the best practice is to apply them at full rate at once. In vegetable rotation, lime is applied to cabbage or root crops. In grain and fodder crop rotations, liming is used primarily on fields to be sown with plants most sensitive to acidity, namely, clover, root crops, wheat, and pulses.

Flax and potatoes respond unfavourably to heavy liming especially on inadequately cultivated, light and underfertilized soils. The negative effect of high lime rates on flax and potatoes is especially pronounced when these crops are planted several years after liming. To avoid this, it has been recommended to reduce the lime rates in rotations with flax and potatoes by one quarter or one third on moderately heavy and heavy loams and by one half on light sandy and sandy loam soils. However, application of lime at lower rates does not reduce soil acidity in any perceptible way, yields of other rotating crops are decreased, and inorganic fertilizers become less effective.

If flax and potatoes are planted not later than on the third or fourth year after liming, the lime rate on light soils can be reduced only by 25 per cent, while on moderately heavy and heavy soils liming should proceed at full rate. Then, liming produces no ill effect on flax and potatoes, while ensuring higher yields of clover, winter wheat, and other crops sensitive to acidity.

Liming at higher rates should preferably be done with fertilizers containing magnesium or shale ash and metallur-

gical slags. Application of these lime materials even at less than full rates increases the quantity and improves the quality of flax and potato yields.

When lime carbonate is applied at full rate, liming should be combined with the introduction of manure and inorganic fertilizers into the crop rotation, with boron fertilizers being placed under flax and potatoes.

Application of potassium fertilizers at high rates is especially important. When sufficient amounts of organic and inorganic fertilizers are applied with a high rate of potassium, liming at full $CaCO_3$ rates can also be performed in crop rotations with flax and potatoes. At specialized potato farms (growing commercial or seed potatoes), light sandy and sandy loam moderately or weakly acidic soils as well as loamy soils with a weakly acidic reaction (pH 5 and above) are not treated with lime.

In crop rotations with annual lupine or seradella grown as green manure, liming is done when these plants are ploughed under.

On natural haylands and pastures, lime fertilizers are spread on the surface, then harrowed late in autumn or early in spring at a rate corresponding to one half or three fourths of hydrolytic acidity. During radical pasture improvement, lime is applied at full rate with ploughing. Lime minimizes infestation with acid-tolerant cereal grasses and weeds, increasing instead the population of legumes, improving the growth and development of grazing crops, and ultimately enhancing the yield and nutritive value of hay or green fodder.

Liming is a prerequisite for creating cultivated pastures on acid soils.

When spread on the surface, lime acts rather slowly and neutralizes acidity only in the topsoil. On the other hand, when ploughed under during radical pasture improvement, its action is intensified.

When orchards or nurseries are established, lime is applied at full rate with deep ploughing. If no lime has been used during establishment of an orchard, it is applied at full rate around individual trees.

4.2 Application of Gypsum to Alkaline Soils

Application of gypsum ($CaSO_4 \cdot 2H_2O$) is intended for chemical amelioration of alkaline soils. These soils are characterized by high sodium content in the absorbing complex and alkaline reaction of the soil solution. Depending on the exchangeable sodium content, such soils are divided into *weakly alkaline* (5-10% Na), *moderately alkaline* (10-20% Na), and *strongly alkaline* (more than 20% Na) soils, the latter also being known under the name "solonetz". Calcium and magnesium in alkaline soils account for the rest of the exchange capacity. Sometimes, exchangeable sodium in alkaline soils accounts for as high as 80 and more per cent of their exchange capacity. Water-soluble salts in alkaline soils are usually present in small amounts not exceeding 0.25 per cent by weight of the soil. The unfavourable physical, physicochemical, and biological properties of such soils along with their low fertility stem primarily from the high content of exchangeable sodium in them.

When saturated with sodium (in the absence of water-soluble salts), mineral and organic colloids of the soil become readily peptized, being partially converted into sol, which is why soil aggregates are pulverized, and the peptized colloids are leached from the top into lower layers, forming a solid alkaline horizon. Solonetz soils are also classified as shallow or *crustal*, in which the alkaline horizon occurs at a depth of not more than 7 cm, *mediocolumnar*, at a depth of 7 to 15 cm, *deep-columnar*, at a depth below 15 cm. Alkaline soils are characterized by high tenacity, pronounced dispersion, and unfavourable water and air regimes. When moist, the alkaline horizon swells perceptibly, becomes almost impermeable to water, sticky and smeary, and, when dry, it turns to a compact hard mass difficult to till. The alkaline horizon does not let the root system of plants penetrate deep into the soil. As a result of the exchange reaction between exchangeable sodium and calcium bicarbonate or carbonic acid, sodium carbonates ($NaHCO_3$ and Na_2CO_3) form in the soil solution of alkaline soils, these salts accounting for high alkalinity of the solution (pH 9 and above) by virtue of their

being hydrolytically alkaline:

$$(\text{soil})^{\text{Na}}_{\text{Na}} + \text{Ca}(\text{HCO}_3)_2 \rightleftarrows (\text{soil})\ \text{Ca} + 2\text{NaHCO}_3$$

$$(\text{soil})^{\text{Na}}_{\text{Na}} + \text{H}_2\text{CO}_3 \rightleftarrows (\text{soil})^{\text{H}}_{\text{Na}} + \text{NaHCO}_3$$

The resulting soda cannot be removed from alkaline soils by leaching because, as long as exchangeable sodium is present there, it re-emerges as a consequence of interaction with calcium bicarbonate or carbonic acid always present in the soil solution. The excessively alkaline reaction of the solution is detrimental to most crops and soil microorganisms. An alkaline reaction upsets the metabolism in plants and makes the compounds of iron, manganese, boron, calcium, and magnesium phosphates in the soil less readily soluble and available. Crop yields on alkaline soil are low with poor crop quality.

Alkaline soils occur widely in the semidesert and steppe zones, being predominant among chestnut soils and less common among chernozems (primarily in the deltas of the Dniepr and Don rivers and in Western Siberia). They seldom occupy vast, continuous tracts of land, occurring mostly in the form of spots of various sizes (from several metres to hundreds of metres in diameter) among chestnut or chernozemic soils.

Sizable areas of alkaline soils can be found in Western Siberia, Kazakhstan, and Transcaucasia. They are especially abundant in irrigation farming regions.

To radically improve alkaline soils, one must remove soda from them, replace exchangeable sodium by calcium, leach out the forming sodium sulphate, and break the compact alkaline horizon.

From the standpoint of amelioration, alkaline soils are divided into two groups:

1. Steppe alkaline soils occurring in the chestnut and brown soil zones. They are characterized by a neutral reaction and deep underground water, which is why salts are not transferred by the latter into the root layer. Such soils can be improved even without gypsuming, by deep tillage to involve the soil-derived calcium ($CaCO_3$ or $CaSO_4$ of the underlying horizon) into the amelioration process.

2. Meadow alkaline soils occurring primarily in the chernozem belt (Ukraine, Transuralia, Western Siberia, Kazakhstan). Their reaction is alkaline, and the water table is shallow, which is why these soils are prone to secondary alkalinization. Amelioration of such soils calls for gypsum application in combination with deep tillage, application of organic and inorganic fertilizers, irrigation, and other farming practices.

Gypsum must be applied to ameliorate alkaline soils containing exchangeable sodium in an amount exceeding ten per cent of the overall exchange capacity.

Weakly alkaline soils (less than 10% Na) are reclaimed agrobiologically, that is, by three-depth ploughing with heavy manuring and planting of alfalfa and other crops accumulating soil-derived calcium in their roots. After their pecomposition, the calcium is released and displaces sodium from the absorbing complex. This process is particularly intensive under irrigation.

4.2.1 Changes Induced in the Soil by Gypsum

When gypsum is applied, soda is removed from the soil solution, and exchangeable sodium is replaced by calcium with formation of a readily soluble neutral salt, namely, sodium sulphate:

$$Na_2CO_3 + CaSO_4 = CaCO_3 + Na_2SO_4$$

$$(soil)^{Na}_{Na} + CaSO_4 = (soil)\ Ca + Na_2SO_4$$

Small amounts of Na_2SO_4 formed in the soil solution do not produce any harmful effect on plants. However, when gypsum is applied to soils containing sodium in amounts exceeding 20 per cent of the exchange capacity, large quantities of Na_2SO_4 form in the soil, which must be removed by irrigation.

Gypsum incorporated into an alkaline soil neutralizes its alkaline reaction. The replacement of exchangeable sodium by calcium is accompanied by coagulation of soil colloids; the active humus resulting from decomposition of plant residues bonds soil particles together in the presence of calcium, the soil acquires a compact aggregate structure, its

physical properties, water permeability and aeration are improved, and the soil becomes easy to till.

By neutralizing alkalinity and improving the physical properties of the soil, gypsum creates favourable conditions for the development and activity of soil microorganisms.

Thus, gypsum application enhances the fertility of alkaline soils and even renders them suitable for cultivation of demanding crops.

4.2.2 Effectiveness of Gypsum Application

According to the results of many experiments, the average yield increase due to gypsuming is 3 to 6 centners of grain per hectare in the chernozem belt without irrigation and 2 to 7 centners per hectare in the chestnut soil zone. Because gypsum interacts slowly with the soil, its effect manifests itself gradually, steadily increasing within the first few years after application. Without irrigation, gypsum application becomes fully effective after four to five years. A prerequisite for rapid improvement of alkaline soils by gypsum is sufficient moisture content in the soil. In dry soil, dissolution of gypsum, substitution of calcium for exchangeable sodium, and removal of the latter from the topsoil do not occur or are extremely slow. Therefore, in dry agriculture, the effectiveness of gypsum application is increased by combining it with deep tillage, snow retention, and other farming practices conducive to removal of sodium from the root layer of the soil. The properties of alkaline soils treated with gypsum change much more rapidly and drastically under irrigation, hence, the effectiveness of gypsuming is much higher in this case.

In order to avoid secondary salinization of alkaline soils as a result of irrigation, special measures are taken to prevent seepage of water from irrigation canals, and irrigation is combined with drainage.

The effectiveness of gypsum application is significantly enhanced when it is combined with deep tillage (Table 4.16).

The effectiveness of gypsum application to alkaline soils is also perceptibly increased by combining it with manuring and application of nitrogen and phosphorus fertilizers (Table 4.17).

Table 4.16. Alfalfa Hay Yield (in centners per hectare) (field test at the Volgograd Experimental Station)

Gypsum rate per hectare	Tillage to a depth of	
	20 cm	30 cm
No gypsum	11.0	12.1
3 tons of gypsum	13.7	17.9
5 tons of gypsum	13.7	31.0
7 tons of gypsum	22.6	32.0

Table 4.17. Effect of Gypsuming in Combination with Manuring and Application of Inorganic Fertilizers on Spring Wheat Yields (experiments at the Siberian Research Institute of Agriculture)

Experimental conditions *	Mediocolumnar solonetz		Deep-columnar solonetz	
	Yield (cent/ha)	Yield increment (cent/ha)	Yield (cent/ha)	Yield increment (cent/ha)
Control	1.0	—	9.9	—
5 tons of gypsum	—	—	12.5	2.6
10 tons of gypsum	9.3	8.3	14.5	4.6
Control	1.7	—	4.5	—
5 tons of gypsum + $N_{60}P_{60}$	9.5	7.8	12.6	8.1
5 tons of gypsum + 40 tons of manure	15.4	13.7	16.2	11.7
10 tons of gypsum + 40 tons of manure	12.1	10.4	18.6	14.1

* The fertilizer rates are given per hectare.

The best form of nitrogen fertilizers for alkaline soils is ammonium sulphate, while that of phosphorus fertilizers is ordinary superphosphate.

Changes induced by gypsum in the soil persist over many years, hence, prolonged positive effect of gypsum application on the yields of farm crops.

4.2.3 Materials Used for Soil Gypsuming

Fresh gypsum powder ($CaSO_4 \cdot 2H_2O$) is produced by crushing freshly quarried gypsum. The powder is white or grey, contains 71-73% $CaSO_4$, and is poorly soluble in water (but better than limestone). Its fineness is extremely important. According to the standard currently in force, all gypsum particles must pass through a sieve with 1-mm mesh and at least 70 to 80 per cent through a sieve with 0.25-mm mesh. The moisture content in crushed gypsum must not exceed 8 per cent, otherwise it tends to lump in storage.

Phosphogypsum is a by-product of phosphorus fertilizer (double superphosphate and precipitate) processing. Being an extremely fine grey or white powder, it contains 70-75% $CaSO_4$ and a small amount of phosphorus (2-3% P_2O_5), which makes it superior to natural gypsum. Gypsum and phosphogypsum should be stored dry indoors.

Argillaceous gypsum is extracted from natural deposits; it is naturally loose, requires no crushing, contains 60-90% $CaSO_4$ and 1-11% clay.

4.2.4 Gypsum Application Rates, Times, and Techniques

Gypsum is applied at rates sufficient for substitution of calcium for excess exchangeable sodium. The gypsum rate is determined using the following formula:

$$CaSO_4 \cdot 2H_2O \text{ rate (t/ha)} = 0.086 \text{ (Na} - KT) Hd$$

where 0.086 corresponds to 1 meq $CaSO_4 \cdot 2H_2O$ (in g); H is the depth of the layer to be treated (in cm); d is the volume weight of the treated soil layer; Na is the total exchangeable sodium content (in meq/100 g of soil); T is the exchange capacity of the treated soil layer (in meq/100 g of soil); and K is the tolerable content of exchangeable sodium in the soil (in fractions of T).

Gypsum application does not call for complete displacement of exchangeable sodium from the soil. According to Antipov-Karataev, the permissible amount of exchangeable sodium that does not produce any adverse effect on soil properties constitutes 10 per cent of the overall exchange capacity (or $0.1T$). The difference between the total content

of exchangeable sodium (Na) and its tolerable content (Na — KT) represents the quantity of the exchangeable sodium to be replaced by calcium. To replace excess exchangeable sodium in 1 g of soil requires $\frac{0.086\,(\mathrm{Na}-KT)}{100\ t}$ grams of gypsum; to displace excess sodium from a 1 cm thick soil layer over an area of 1 ha takes $\frac{0.086\,(\mathrm{Na}-KT)\ 100\,000\,000}{100\times 1\,000\,000}$ or (after reduction) $0.086 \times (\mathrm{Na} - KT)$ tons of gypsum per hectare, while removal of excess exchangeable sodium from the entire soil layer to be treated, having volume weight d, requires $0.086\ (\mathrm{Na} - KT)\ Hd$ tons of gypsum per hectare.

For example, the gypsum rate for amelioration of an alkaline soil with $T = 20$ meq, (Na) = 4 meq, $H = 20$ cm, and $d = 1.8$ is $0.086\ (4 - 0.1 \times 20)20 \times 1.8 = 6.2$ t/ha.

If the exchangeable sodium content in the soil is unknown, the following approximate gypsum rates can be used (in t/ha): one to three for alkaline soils in the chestnut and brown soil zone, three to five for medio- and deep-columnar alkaline soils, five to eight for crustal (chloride-sulphate) alkaline soils, three to four for medio- and deep-columnar alkaline soils in the chernozem belt (five to ten in the presence of soda), and eight, ten, or more for crustal sodic soils (three to four if the alkalinity is mild). Gypsum application to moderately alkaline soils seldom produces a consistent effect. High gypsum rates may be applied gradually, over a period of two to eight years. In irrigated areas, the gypsum rates are reduced by 25 to 30 per cent. Alkaline soils occur in spots among others. If they account for less than 30 per cent of the total area, gypsum is applied only to the spots, but if heavily alkaline spots occupy more than 30 per cent of the area and are surrounded by moderately alkaline soils, the entire area is treated but at different rates.

The ameliorating effect of gypsum depends on the degree of its mixing with the soil. Therefore, gypsum is always incorporated by deep ploughing in autumn so that the alkaline horizon could be better mixed with gypsum and with the layer above. Shallow crustal alkaline soils are treated after ploughing, gypsum being incorporated with the aid of a cultivator. In the case of medio- and deep-columnar solonetz soils where the alkaline horizon is at a depth of 7 to

20 cm, gypsum is applied twice: first under plough with a colter, then under cultivator after ploughing. The more the alkaline horizon is exposed during ploughing, the more gypsum is applied after it. On deep-columnar solonetz soils where the alkaline horizon occurs at a depth not exceeding 20 cm, all of gypsum is applied before ploughing, then incorporated by a plough with a colter.

Alkaline soils are also ameliorated by methods other than gypsum application. In some alkaline soils, the alkaline horizon at a depth of 30 to 45 cm is underlaid by gypsiferous layers. In such cases, the gypsum below the alkaline horizon is used for self-gypsuming: alkaline soils are tilled by a deep plough to a depth of 35 to 50 cm, whereby the gypsiferous layer is upturned (completely or partially) and mixed with the alkaline horizon. The resulting Na_2SO_4 is removed by irrigation.

For reclamation of steppe medio- and deep-columnar alkaline soils of the chestnut soil zone, it has been recommended to use the calcium carbonate present in the subalkaline horizons. However, $CaCO_3$ dissolves in water much more reluctantly than $CaSO_4$. Its solubility and ameliorating effect increase with the concentration of carbon dioxide in the soil solution as a result of activation of soil microorganisms and CO_2 release by plant roots. Carbonic acid converts calcium carbonate into soluble calcium bicarbonate, and calcium displaces exchangeable sodium from the alkaline soil. The ameliorating effect of calcium carbonate is enhanced by resorting to diverse farming practices, including deep ameliorative tillage of the soil (trench or subbase ploughing to a depth of 35 to 40 cm with simultaneous subsoiling by additional 15 to 20 cm), a complex of procedures aimed at increasing the moisture content in the soil (irrigation, snow retention, forest strips, bare and coulisse fallows), application of organic and inorganic fertilizers, planting alfalfa and other drought-resistant and salt-tolerant crops amending alkaline soils in order to increase the content of organic matter in the soil and activate microbiological processes in it.

Alkaline soils occurring as small spots among calcium-rich chernozems can be improved by earthing, that is, by hauling in the nearby chernozem and spreading it over the spots. In this case, the alkaline layer is diluted, and exchan-

geable sodium is partially replaced by the calcium derived from the hauled chernozem. According to the method developed by Orlovskii, chernozem is hauled to alkaline spots several times: each time, it is spread in a layer one to one and a half centimetres thick, the total layer built up throughout a rotation cycle reaching 6 to 9 cm in thickness.

A quicker way to radically improve alkaline soils by earthing has been proposed by the Institute of Agriculture in the Black-Earth Zone in collaboration with the Soil Institute. According to this method, the surface of alkaline spots is covered with a 15 to 20 cm thick layer of the nearby calcium- and humus-rich chernozem hauled in by a scraper in a single trip. Such an amount of chernozem brings about 10 tons of calcium to a hectare, part of this calcium being entrained by the downward flow of soil moisture and becoming involved in the amelioration of the underlying alkaline soil.

4.2.5 Using Gypsum as a Fertilizer

Gypsum is used not only for chemical amelioration of alkaline soils, but also as a calcium- and sulphur-containing fertilizer on soils devoid of exchangeable sodium.

Sulphur is an essential nutrient for plants and plays an important role in their life. Sulphur deficiency inhibits the growth and development of plants and considerably reduces crop yields. Sulphur is taken up from the soil in the form of the SO_4^{2-} anion derived from various sulphates, such as $CaSO_4$, $MgSO_4$, K_2SO_4, $(NH_4)_2SO_4$, and others. Plants may also take up sulphur via leaves from air, in the form of sulphur dioxide (SO_2). Usually, only a small amount of this element is present in plants in inorganic form, primarily as $CaSO_4$, the major part of absorbed sulphur is reduced in plant tissues and becomes a component of various organic compounds: proteins, some vitamins, enzymes, vegetable oils, and the like. Most of sulphur in plants becomes a constituent of proteins.

Since most of sulphur present in plants forms part of proteins, its content in seeds and leaves is higher than in stalks and roots. For example, the roots of sugar beet contain about 0.2% SO_3 in terms of dry matter, while in the tops, its

content is up to 1.0%; in potatoes, tubers contain about 0.35% SO_2, while the haulm contains 0.55%; in grain crops, straw contains 0.12% SO_2, while the kernels contain 0.3 to 0.45%; the seeds of legumes contain much more sulphur (0.6-0.85%) than the kernels of cereals.

Sulphur is a constituent of amino acids, such as methionine, cystine, and cystein, which are essential components of protein molecules. Cystine contains the disulphide (—S—S—) group, while cystein contains a sulphydryl (—SH) one.

When oxidized in plants, cystein is readily transformed to cystine, which is easily reduced back to cystein. The mutual transformations of the disulphide and sulphydryl groups in the "cystine-cystein" system account for the active involvement of these amino acids in the redox processes occurring in plant cells. Cystein also forms part of the tripeptide glutathione, which is an activator of certain ensymes. Sulphur is also present in vitamins, such as thiamin (B_1) and biotin, which play an important role in plant metabolism.

Tiamin is a constituent of some enzymes catalyzing decarboxylation of organic and amino acids, while biotin takes part in deamination and decarboxylation of certain amino acids. Hence, sulphur plays a major role in carbohydrate and nitrogen metabolism in plants.

Sulphur can also be found in some other specific organic compounds: mustard oils forming in the seeds of cruciferous plants (mustard, rape, etc). and garlic oils forming in plants belonging to the lily family (particularly, onions and garlic).

Sulphur is present in greatest amounts in leguminous and cruciferous plants and in much smaller amounts in cereals and potato. The total removal of sulphur by grain crops (20 cent/ha) and potatoes (200 cent/ha) amounts to 7-15 kg, 20 to 30 kg being removed by leguminous grasses, 30 to 40 kg by root crops, and 50 to 80 kg by cabbage.

Most of sulphur is concentrated in crop residues, therefore, rational utilization of the latter will allow the bulk of the sulphur taken up by plants to return into the soil.

Soils usually contain sufficient quantities of sulphur. Most of it (up to 70-90%) is present in a virtually unavailable organic form, hence, the higher the humus content in the soil, the greater the overall reserves of sulphur in it. The sulphur present in the organic matter of the soil or in organic

fertilizers and crop residues incorporated into the soil becomes available for plant nutrition only after their decomposition and mineralization. It should also be mentioned that sulphur bacteria oxidize sulphur to SO_4^{2-}, whereby various sulphates form in the soil.

The quantity of available inorganic sulphur compounds in the soil is usually small. Every year, soils receive a certain amount of sulphur in the form of sulphur dioxide (SO_2) from air, especially in industrially developed regions. When fuel is burnt at industrial enterprises, SO_2 is released into the atmosphere, then finds its way into the soil with precipitations. In addition, sulphur is incorporated with manure and some inorganic fertilizers, such as ammonium sulphate, potassium sulphate, sulpomag (sulphate of potash-magnesia), and ordinary superphosphate containing more than 40% gypsum. Therefore, on most soils crops are never deficient in sulphur. However, on humus-poor soddy podsolic soils, especially when little manure or sulphur-containing fertilizers are applied, addition of this nutrient ensures high yields of legumes, grasses, and other crops.

The sulphur requirements of plants and the need in additional incorporation of this nutrient into the soil will increase with extending production and application of sulphur-free high-analysis (concentrated) fertilizers, as well as with the overall increase in fertilizer rates and the concomitant yield removal of sulphur.

Gypsum as a fertilizer containing calcium and sulphur is applied primarily to leguminous grasses (clover and alfalfa). The positive effect of gypsum on these crops resides not only in improved supply of calcium and sulphur, but also in increased availability of the soil-derived potassium as a result of its displacement from the absorbing complex by the fertilizer calcium. Besides, application of gypsum raises the concentration of calcium in the soil solution, which is why clover and alfalfa become more tolerant to acidic reaction.

In the case of clover and alfalfa, gypsum is applied to the surface in autumn (in arid regions) or over growing grasses in spring. Gypsum is applied at a relatively low rate, i.e. anywhere from three to five centners per hectare. Its effect on legume yields is especially pronounced on soddy podsolic clayey and loamy soils. On soddy podsolic sandy loam, grey

forest soils, and chernozems, the yield increase due to gypsum is not as high. According to the results of field experiments, the average clover hay yield increase due to gypsum was 16.2 centners per hectare on heavy soddy podsolic loams, 11.1 centners on moderately heavy and light loams, 7.2 centners on sandy loams, and 6.5 centners on grey forest soils and leached chernozems. Application of ordinary superphosphate at high rates mitigates the effect of gypsuming on clover and alfalfa yields.

Chapter 5

Nitrogen Fertilizers

According to their chemical composition, all fertilizers are divided into organic and inorganic ones, and, depending on their origin and sources, they may be commercial (nitrogen, phosphorus, potassium, compound, and micronutrient fertilizers) and domestic (manure, peat, ash, etc.).

Inorganic fertilizers contain nutrients primarily in the form of various mineral salts. Depending on the type of nutrients and their content, fertilizers are further subdivided into two groups. Simple, or single, fertilizers include nitrogen, phosphorus, potassium, and some micronutrient (boron, molybdenum, etc.) ones. Compound, or multiple-nutrient, fertilizers contain each two or more basic nutrients.

5.1 Nitrogen in Plant Nutrition

Nitrogen is one of the basic plant nutrients. It is built into the body of all simple and conjugated proteins that are major constituents of plant cell cytoplasm and forms part of nucleic acids (ribonucleic, or RNA, and deoxyribonucleic, or DNA) playing a vital role in the metabolism of living organisms. Nitrogen is present in chlorophyll phosphatides, alkaloids, enzymes, and many other organic substances of plant cells.

The chief source of nitrogen for plant nutrition is nitrates and ammonium salts.

The inorganic forms of nitrogen taken up by plants undergo a complex cycle of transformations ultimately leading to its incorporation into protein molecules. Proteins are synthesized from amino acids which, in turn, result from interaction between ammonia and the keto group of a respective organic acid (*amination*).

Subject to direct enzyme-assisted amination are ketocarboxylic acids, such as pyruvic, oxaloacetic, α-ketoglutaric,

forming in plants as a result of carbohydrate degradation, in the course of anaerobic respiration, or at the initial stage of aerobic respiration. Direct amination of keto acids with ammonia is the main pathway of amino acid synthesis in plants.

Consequently, synthesis of amino acids requires a reduced form of nitrogen. Nitrates and nitrites are not capable of entering into a reaction with the keto groups of organic carboxylic acids which are first reduced to ammonia in plant tissues for the amino acids to form. If plants contain a sufficient amount of carbohydrates, nitrates are reduced to ammonia already in roots. The process of enzymic reduction of nitrates, which occurs in plants by virtue of carbohydrate oxidation, involves a number of intermediate compounds and is catalyzed by several enzymes:

$$\underset{\text{nitrate}}{HNO_3} \rightarrow \underset{\text{nitrite}}{HNO_2} \rightarrow \underset{\text{hyponitrite}}{(HNO)_2} \rightarrow \underset{\text{hydroxylamine}}{NH_2OH} \rightarrow \underset{\text{ammonia}}{NH_3}$$

At the first stage of the process, nitrates acted upon by the enzyme nitrate reductase are reduced to nitrites:

$$HNO_3 + H_2 \rightarrow HNO_2 + H_2O$$

Subsequently, nitrite reductase catalyzes reduction of the nitrite to hyponitrite:

$$2HNO_2 + 2H_2 \rightarrow H_2N_2O_2 + 2H_2O$$

Then, hyponitrite reductase causes attachment of two more hydrogens, yielding hydroxylamine:

$$H_2N_2O_2 + 2H_2 \rightarrow 2NH_2OH$$

The subsequent reduction of hydroxylamine with the aid of hydroxylamine reductase results in ammonia:

$$NH_2OH + H_2 \rightarrow NH_3 + H_2O$$

The enzymes causing nitrates to be reduced to ammonia are essentially metalflavoproteins. The enzyme involved in the reduction of nitrates to nitrites requires molybdenum; the enzyme catalyzing the reduction of nitrite to hyponitrite and that of hyponitrite to hydroxylamine requires copper, iron, and magnesium, while manganese and magnesium are required for hydroxylamine to be reduced to ammonia.

Of all the above elements, molybdenum is particularly important from the standpoint of nitrate reduction catalysis.

Nitrate nitrogen can be accumulated in plants in large amounts without harming them. However, excess nitrates in fodder, vegetables, and other products of plant origin are harmful to the animals and humans who eat these products.

Free ammonia is usually present in higher plants in insignificant amounts; its excess leads to plant poisoning, especially in the case of carbohydrate deficiency.

When carbohydrates are sufficient, the ammonia nitrogen taken up by plants from the soil and resulting from nitrate reduction combines with organic keto acids (oxaloacetic, ketoglutaric, and fumaric) to form primary amino acids, namely, aspartic and glutamic ones.

The reaction yielding these amino acids proceeds in two steps. In the first step, an imino acid and water form from ammonia and the keto acid, then the imino acid is reduced to an amino acid. For example, while attaching ammonia and splitting off water, oxaloacetic acid is transformed to iminoxaloacetic acid, which is then reduced to aspartic acid:

$$\underset{\text{oxaloacetic acid}}{\text{COOH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOH}} \xrightarrow[-\text{H}_2\text{O}]{+\text{NH}_3} \underset{\text{iminoxaloacetic acid}}{\text{COOH}\cdot\text{C}=\text{NH}\cdot\text{CH}_2\cdot\text{COOH}} + 2\text{H} \rightarrow \underset{\text{aspartic acid}}{\rightarrow \text{COOH}\cdot\text{CHNH}_2\cdot\text{CH}_2\cdot\text{COOH}}$$

Similarly, ketoglutaric acid and ammonia yield glutamic acid:

$$\underset{\text{ketoglutaric acid}}{\text{COOH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}} \xrightarrow[-\text{H}_2\text{O}]{+\text{NH}_3} \underset{\text{iminoglutaric acid}}{\rightarrow \text{COOH}\cdot\text{C}=\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}} + 2\text{H} \rightarrow \underset{\text{glutamic acid}}{\rightarrow \text{COOH}\cdot\text{CHNH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}}$$

Aspartic acid may also result from direct attachment of ammonia to fumaric acid:

$$\underset{\text{fumaric acid}}{\text{COOH}\cdot\text{CH}=\text{CH}\cdot\text{COOH}} \underset{\text{aspartase}}{\overset{+\text{NH}_3}{\rightleftharpoons}} \underset{\text{aspartic acid}}{\text{COOH}\cdot\text{CH}_2\cdot\text{CHNH}_2\cdot\text{COOH}}$$

The reaction yielding amino acids through direct amination of keto acids is extremely important in plant metabolism. It is indicative of a relationship between carbohydrate and protein metabolisms. Aspartic and glutamic acids are capable of transferring their amino groups to other keto acids by way of enzymic transamination. The transamination process consists in transfer of the amino group of the amino acid (donor) to the keto acid (acceptor). For instance, pyruvic acid accepts the amino group from aspartic or glutamic acid to give alanine. Glutamic and oxaloacetic acids yield aspartic and α-ketoglutaric acids through transamination, whereas the latter two yield glutamic and oxaloacetic acids.

1. $\underset{\text{aspartic acid}}{COOH\cdot CH_2\cdot CHNH_2\cdot COOH} + \underset{\text{pyruvic acid}}{CH_3\cdot CO\cdot COOH} \xrightarrow{\text{aminotransferase}}$

$$\rightarrow \underset{\text{alanine}}{CH_3\cdot CHNH_2\cdot COOH} + \underset{\text{oxaloacetic acid}}{COOH\cdot CH_2\cdot CO\cdot COOH}$$

2. $\underset{\text{glutamic acid}}{COOH\cdot CH_2\cdot CH_2\cdot CHNH_2\cdot COOH} + \underset{\text{pyruvic acid}}{CH_3CO\cdot COOH} \overset{\text{aminotransferase}}{\rightleftharpoons}$

$$\rightleftharpoons \underset{\text{alanine}}{CH_3\cdot CHNH_2\cdot COOH} + \underset{\text{α-ketoglutaric acid}}{COOH\cdot CH_2\cdot CH_2\cdot CO\cdot COOH}$$

3. $\underset{\text{glutamic acid}}{COOH\cdot CH_2\cdot CH_2\cdot CHNH_2\cdot COOH} + \underset{\text{oxaloacetic acid}}{COOH\cdot CO\cdot CH_2\cdot COOH} \overset{\text{aminotransferase}}{\rightleftharpoons}$

$$\rightleftharpoons \underset{\text{α-ketoglutaric acid}}{COOH\cdot CH_2\cdot CH_2\cdot CO\cdot COOH} + \underset{\text{aspartic acid}}{COOH\cdot CHNH_2\cdot CH_2\cdot COOH}$$

The transamination reaction was discovered in 1937 by the Soviet scientists Braunshtein and Kritsman. The transfer of amino groups from amino to keto acids provides a pathway for synthesis of most amino acids forming part of protein. In plants, glutamic and aspartic acids lend themselves readily to transamination, which is indicative of their importance in metabolism. Additional sources of amino groups for transamination involving keto acids may be γ-aminobutyric acid and amides of aspartic and glutamic acids, i.e. asparagine and glutamine. Transamination is essential for protein synthesis and also for *deamination* of amino acids.

Deamination implies removal of the amino group from an amino acid, resulting in ammonia and a keto acid. The latter is converted by plants into carbohydrates, fats, and other substances; as far as ammonia is concerned, it again enters into a reaction of direct amination of keto acids, yielding respective amino acids. Moreover, aspartic and glutamic acids may combine with another ammonia molecule, whereby amides of aminodicarboxylic acids (asparagine and glutamine) are formed:

$$\underset{\text{aspartic acid}}{COOH \cdot CH_2 \cdot CHNH_2 \cdot COOH} + NH_3 \xrightarrow[-H_2O]{} \underset{\substack{\text{amide of aspartic acid} \\ \text{(asparagine)}}}{CONH_2 \cdot CH_2 \cdot CHNH_2 \cdot COOH}$$

The monamide of glutamic acid (glutamine) is formed in plants in exactly the same manner. Asparagine and glutamine may be accumulated in tissues in large amounts without harming plants.

The physiological role of the above amides has been elucidated by the classic experiments conducted by Pryanishnikov. It has been established that formation of asparagine and glutamine results in neutralization of the ammonia accumulated in the tissues of higher plants in the course of deamination of amino acids or in the case of more than adequate ammonia nutrition with carbohydrate deficiency.

In some plants (horsetail, dock, sedges), as a consequence of heavy accumulation of organic acids, ammonia is neutralized through formation of ammonium salts of respective organic acids rather than amides:

$$\underset{\substack{| \\ COOH \\ \text{oxalic acid}}}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}} + NH_3 \rightarrow \underset{\substack{| \\ COOH \\ \text{ammonium oxalate}}}{\begin{matrix} COONH_4 \\ | \\ COOH \end{matrix}}$$

Asparagine and glutamine are also essential for enzymic transamination. This process involves not only aspartic and glutamic acids, but also asparagine and glutamine.

Dicarboxylic amino acids are predominant in vegetable proteins. Therefore, transformations of these amino acids and their amides are of paramount importance in the nitrogen metabolism of plants.

Protein synthesis from amino acids necessitates chemical energy which is produced by plant respiration and is accumulated in the form of high-energy bonds in adenosine triphosphate (ATP). Another major factor of protein synthesis is nucleic acids. They serve as a matrix (framework) in which amino acids are arranged in a certain pattern, being involved in peptide bonding and forming an infinite variety of protein molecules.

The synthesis of proteins in plants goes hand in hand with their degradation into amino acids with elimination of ammonia. Protein hydrolysis is catalyzed by enzymes known as proteases. In the growing organs and young plants, protein synthesis is predominant over their degradation, while in old plants the latter process takes over. As shown by the results of experiments with the nitrogen isotope ^{15}N, the turnover of protein nitrogen is much faster in young as opposed to old plants. The ammonia released in the breakdown of proteins is not accumulated in plant tissues, but is used to form dicarboxylic amino acids and their amides (asparagine and glutamine). Amino acids serve as the starting material for biosynthesis of proteins and a great many other nitrogenous compounds.

The entire complex cycle of synthesis of organic nitrogenous substances in plants has already been shown to begin with ammonia, their breakdown terminating in its formation. This had prompted Pryanishnikov to remark that "ammonia is alpha and omega in the metabolism of nitrogenous substances in plants". The uptake of nitrogen by plants and its involvement in the synthesis of proteins and other organic nitrogenous substances occur throughout the vegetation period but with different intensities at different growth and development stages.

When seeds germinate, the stored proteinaceous substances break down into amino acids. During their subsequent oxidation in individual organs of the sprouts, nitrogen is split off as ammonia which is used to form amino acids (aspartic and glutamic) and amides (asparagine and glutamine) and, in the final analysis, to synthesize proteins and other nitrogen compounds in the newly emerging plant organs. Further, as the root system and photosynthetic surface of leaves are formed, protein synthesis is based on the nitro-

gen taken up from the environment. At the initial stage of growth, plants consume a relatively small amount of nitrogen. However, its deficiency during this period adversely affects the subsequent growth of plants. Nitrogen is taken up and used in the synthesis of amino acids and proteins most intensively at the peak of growth and during formation of vegetative organs, such as stalks and leaves. Throughout the vegetation period, protein synthesis is predominant in the young, growing, organs and gives way to protein degradation as the plant senesces.

In view of the dissimilar pattern and rate of nitrogen metabolism in different parts of a plant, nitrogen is redistributed in the plant organism. Notably, proteinaceous substances in the physiologically aged organs, primarily leaves, undergo breakdown (hydrolysis) with the hydrolysis products being translocated into the young, growing organs. At the seed formation stage, the proteinaceous substances present in leaves degrade intensively, and the degradation products, mainly amino acids, migrate into the maturing seeds where they are again converted into proteins. Hence, the nitrogen content in seeds increases, while that in vegetative organs decreases.

During this period, the uptake of nitrogen from the soil is limited or discontinues altogether. The total nitrogen content varies in different plants and even in different parts of the same plant. Seeds contain more nitrogen than leaves and stalks at the end of the vegetation period, most of it (up to 90%) being localized in protein (Table 5.1).

Vegetable proteins contain an average of 16% nitrogen, or one sixth of their weight. The quality of grain and other farm products is often estimated in terms of "crude protein",

Table 5.1. Nitrogen Content in Different Parts of Plants (% of dry matter)

Plant	Seeds, roots	Straw, tops
Pea	3.6	1.4
Wheat	2.5	0.6
Sugar beet	0.8	1.3

meaning the total amount of nitrogenous compounds in a crop, most of which, in seeds, is protein. The crude protein content is calculated by multiplying the total nitrogen content by 6.25.

Leaves and stalks as well as roots and tubers of crops may contain sizable amounts of non-protein nitrogen. For example, in leaf vegetables, roots of sugar, fodder and table beet, and potato tubers, non-protein nitrogen compounds account, upon reaching economic maturity, for almost half the total content of this element. The vegetative organs richest in nitrogen are leaves, especially young ones, stalks and roots containing less nitrogen. Legumes contain more nitrogen in all organs than cereals.

The conditions of nitrogen nutrition appreciably affect the growth and development of plants. When nitrogen is deficient, their growth is markedly inhibited. The effect of nitrogen deficiency is strongest on the development of leaves: they remain stunted, have a light green colour prematurely turning yellow, while stalks become thin and fail to branch properly. Also inhibited are formation and development of reproductive organs and seeds.

When nitrogen nutrition is normal, the synthesis of proteinaceous substances is intensified, the vitality of the plant organism is enhanced and prolonged, the growth of leaves is accelerated and their senescence is slowed down somewhat. Plants develop sturdy stems and leaves of intensely green colour, grow and tiller well with better formation and development of the reproductive organs. As a result, the yields and protein content of crops increase. However, excessive uptake of nitrogen at the expense of other nutrients, especially during the second half of the vegetation period, delays the maturation of plants, whereby they produce an abundant vegetative mass but little grain or tubers and roots. An increase in the protein content improves the crop quality, but not every increase in the content of nitrogenous compounds enhances the commercial value of crops. For example, excessive nitrogen nutrition by the end of the vegetation period is responsible for heavy accumulation of non-protein nitrogen compounds, primarily amino acids, in sugar beet roots with the result that the sugar yield in their processing is low.

Excessive nitrogen nutrition may also lead to accumulation of nitrates in plants, to concentrations harmful for man and animals.

Crop quality is also dependent on the form in which nitrogen is assimilated by plants. In the case of ammonia nutrition, the reducing capacity of plant cells becomes more pronounced, and more reduced organic compounds are formed (e.g. essential oils in peppermint). On the other hand, in the case of nitrate nutrition, the oxidizing capacity of the cell sap becomes predominant, and more organic acids are produced, for example, citric acid in rustic tobacco (Vladimirov).

The experiments conducted by Pryanishnikov and his pupils have shown that ammonia and nitrates may serve as equivalent sources of nitrogen for plants, provided the external and internal conditions are right. Yet, under certain conditions, NH_4^+ may be a better source than NO_3^- and vice versa.

The response of plants to ammonia and nitrate nitrogens depends on a number of factors: medium pH, presence of associated cations, anions, and ash elements (phosphorus sulphur, potassium, micronutrients) in it, concentration of calcium, magnesium, ammonium salts, and nitrates in the soil solution, and the carbohydrate content in the plants. In the neutral solution, ammonium salts are taken up more, and at an acidic reaction less, vigorously than nitrates. The concentration of associated cations and anions produces a tangible effect on the uptake of ammonia or nitrate nitrogen. In the case of ammonia nutrition, the yield increases with the concentration of calcium, magnesium, and potassium in the nutrient substrate, whereas in the case of nitrate nutrition, adequate supply of plants with phosphorus and molybdenum is more important. Molybdenum deficiency slows down the reduction of nitrates to ammonia, and they tend to accumulate in plant tissues. The uptake of ammonia nitrogen is also strongly dependent on the internal factors, primarily the carbohydrate content in plants. If carbohydrates are deficient, insufficient organic acids, especially α-keto acids which act as acceptors binding ammonia, are formed. Early in their development, plants require increased amounts of nitrogen for expansion of their foliar surface. Yet excess

ammonia nitrogen during germination of carbohydrate-poor seeds (e.g. sugar beet) or at the stage of sprouts that cannot yet fully assimilate nutrients may produce a negative effect. In this case, ammonia nitrogen cannot be fully utilized by plants, being accumulated in their tissues and causing "ammonia poisoning". No such thing may happen in the case of nitrate nutrition. Plants, especially when young and having little carbohydrates in their seeds, are less tolerant to increased concentrations of ammonium salts in the soil solution than to those of nitrates.

The negative effect of excess concentrations of ammonia nitrogen in the solution is particularly manifest when nitrogen fertilizers are drilled during seeding. Therefore, the nitrate rather than ammonia form of fertilizer should preferably be applied at seeding.

5.2 Nitrogen Content in Soils and the Dynamics of Its Compounds

According to Vinogradov, the content of nitrogen in the Earth's crust is 2.3×10^{-2} per cent by weight, its total reserves amounting to tens of billions of tons. Most of nitrogen is present in the soil in the form of complex organic compounds. Besides, part of the nitrogen in the Earth's crust takes the form of non-exchangeable ammonium ions and is retained in the crystal lattice of aluminosilicate minerals. In the arable layer (0 to 25 cm) of various soils, the nitrogen content varies widely (from 0.05 to 0.5%).

The overall nitrogen content in soils depends on the amount of organic matter they contain: nitrogen is most abundant in humus-rich deep chernozems and most scarce in humus-poor soddy podsolic soils and sierozems.

The nitrogen content in the soil also varies perceptibly within the same soil zone. For example, soils of the Non-Black Earth zone in the European part of the Soviet Union have the following average contents of total nitrogen: sandy loam, 0.05 to 0.07%; loam, 0.10 to 0.20%; clays, 0.10 to 0.23%; and peats, 0.6 to 1.0%. The overall nitrogen reserves in a hectare of the arable layer vary from 1.5 tons in

Table 5.2. Nitrogen Content in the Arable Layer of Various Soils

Total nitrogen	Soil			
	soddy podsolic	grey forest	leached chernozem	deep chernozem
Percentage	0.05-0.20	0.20-0.35	0.30-0.45	0.40-0.50
t/ha	1.5-6.0	6-10.5	9-13.5	12-15
Total nitrogen	Soil			
	ordinary chernozem	chestnut	sierozem	red
Percentage	0.25-0.45	0.15-0.25	0.10-0.20	0.20-0.30
t/ha	7.5-13.5	4.5-7.5	3-6	6-9

soddy podsolic sandy loam to 15 tons in deep chernozem (Table 5.2). However, the supply of farm crops with nitrogen depends not so much on its overall content in the soil as on that of the available inorganic compounds. Most of nitrogen in the soil, present in various organic compounds (94-95%) or in the form of ammonium non-exchangeably fixed by argillaceous minerals (3-5%) is completely or almost unavailable. Only a small amount of nitrogen (about 1% of the total content) is found in readily available inorganic forms (NO_3^- or exchangeable NH_4^+). Hence, normal supply of plants with nitrogen is determined by the mineralization rate of nitrogenous organic substances. The decomposition of the latter in the soil can be schematically represented in the following general form:

proteins, humic substances → amino acids, amides → ammonia → → nitrites → nitrates

The breakdown of nitrogenous organic substances of the soil to ammonia is known as **ammonification.** It is initiated by vast groups of aerobic and anaerobic microorganisms, including bacteria, actinomyces, and mold fungi.

Acted upon by the proteolytic enzymes released by these microorganisms, proteinaceous substances are hydrolyzed to

amino acids. The latter are readily assimilated by microorganisms and are deaminated and deamidated under the effect of microbial cell enzymes (deaminases and deamidases). As a result, ammonia is split off amines and amides to form various organic acids which degrade further to simplest compounds, such as CO_2, H_2O, H_2, and CH_4. The evolving ammonia combines with organic and inorganic acids (carbonic, nitric, formic, acetic, etc.) to form respective salts during mineralization of the organic matter in the soil:

$$2NH_3 + H_2CO_3 \quad (NH_4)_2CO_3$$
$$NH_3 + HNO_3 \quad NH_4NO_3$$

Ammonium is adsorbed by soil colloids:

$$(soil)\begin{matrix}Ca\\Ca\end{matrix} + (NH_4)_2CO_3 = (soil)\begin{matrix}NH_4\\NH_4\end{matrix} + CaCO_3$$

Ammonification occurs in all soils at different reactions of the medium, with or without air, although under anaerobic conditions it slows down considerably when the reaction is highly acidic or alkaline. Other factors affecting the ammonification rate include soil temperature, moisture content, and so on. Under anaerobic conditions, nitrogenous organic substances are decomposed to ammonia. Under aerobic conditions ammonium salts are oxidized to nitrates.

Nitrification is effected by a group of specific bacteria for which this oxidation serves as a source of energy. The first to study this process was Vinogradsky. He isolated pure cultures of these bacteria and elucidated the mechanism of nitrification. Involved in the oxidation of ammonium salts to nitrous acid (first stage) are bacteria of the genera *Nitrosomonas*, *Nitrosocystis*, and *Nitrosospira*, while the oxidation to nitric acid (second stage) is initiated by bacteria of the genus *Nitrobacter*. The nitrification process can be written as follows:

$$2NH_3 + 3O_2 = 2HNO_2 + 2H_2O \text{ (first stage)}$$
$$2HNO_2 + O_2 = 2HNO_3 \text{ (second stage)}$$

Nitrification seems to be based on the dehydrogenation of ammonia initiated by dehydrogenase, whereas the combin-

ing of nitrogen with oxygen is effected by respective oxidases. It has been established that nitrification is a multistep process. First, ammonium is oxidized to hydroxylamine, which is oxidized via several intermediate products to HNO_2 oxidized subsequently to HNO_3:

$$NH_3 \xrightarrow{(+H_2O)} NH_4OH \xrightarrow{(-2H)} \underset{\text{hydroxylamine}}{NH_2OH} \xrightarrow{(-2H)} HNO \xrightarrow{(+H_2O)}$$

$$\rightarrow NH(OH)_2 \xrightarrow{(-2H)} HNO_2 \rightarrow HNO_3$$

The nitric acid appearing in the soil as a result of nitrification is neutralized by calcium or magnesium bicarbonate or by exchangeable bases of the soil:

$$2HNO_3 + Ca(HCO_3)_2 = Ca(NO_3)_2 + 2H_2CO_3$$

$$2HNO_3 + (soil)\begin{matrix}Ca\\Ca\end{matrix} = (soil)\begin{matrix}H\\H\end{matrix} + Ca(NO_3)_2$$

In the case of adequate aeration, a moisture content of 60 to 70 per cent, capillary moisture capacity, a temperature of 25 to 32 °C, and pH 6.2-8.2, nitrification proceeds at a fast rate, and the bulk of ammonia nitrogen is rapidly oxidized to nitrates. According to Lebedyantsev, with sufficient reserves of nitrogenous organic substances in the soil, nitrification may yield up to 100 mg of nitric acid per kg of the soil (300 kg/ha) each year.

The mineralization rate of the organic matter is dissimilar in different soils. It is higher in soddy podsolic soils, as compared to chernozems where the decomposition of the organic matter is slower.

However, more nitrates form in chernozems than in soddy podsolic soils. Chernozems are richer in organic matter, have a thick humic layer, and provide more favourable conditions, as opposed to soddy podsolic soils, for nitrification (more nitrifying microorganisms, higher temperature, and neutral or almost neutral soil reaction). Soddy podsolic soils contain little humus, and the conditions for nitrification are less favourable. Acidic reaction, poor aeration, excess moisture, and a low soil temperature slow down the mineralization processes, which discontinue at the ammonia formation step. Because of the unfavourable conditions for the

activity of nitrifying bacteria, nitrification is suppressed. Its rate is especially slow in early spring when the microbiological activity is inhibited by low soil temperature and anaerobic conditions brought about by saturation of the soil with melt water. As the soil gets warmer, the nitrate content increases and reaches its maximum in summer, then goes down again towards autumn.

The rate of oxidation of ammonia to nitrates is also influenced by tillage, liming, and fertilizers. Almost no nitrates accumulate in a soil occupied by plants, particularly cereals, because of the slow nitrification (as a result of compaction of the soil) and absorption of nitrate nitrogen by roots; in this case, its content in the arable layer is low.

Tillage of soils, especially heavy ones, intensifies the nitrification process. A similar effect is produced by liming of acid soils. In base-deficient, poorly aerated acid peaty soils as well as inadequately cultivated, calcium-poor acid soddy podsolic soils, nitrification is slow as a rule. Liming reduces soil acidity, activates nitrifiers, and enriches the soil with calcium which is necessary for combining with nitrates to form $Ca(NO_3)_2$. Lime further gains in importance if nitrification involves not only the ammonia resulting from mineralization of organic substances, but also that incorporated into the soil with fertilizers in the form of ammonium sulphate and nitrate. Apart from neutralizing nitric acid, calcium is also needed in the latter case to bind the acid residues from fertilizers.

Organic and inorganic fertilizers enrich the soil with nitrogen and ash elements and also considerably intensify the mineralization processes in it. Introduced with organic fertilizers are organic substances stimulating the activity of microorganisms plus a highly diverse microflora (e.g. with manure) speeding up decomposition of the organic matter in the soil. Inorganic fertilizers intensify the biological processes in the latter since they supply nitrogen, phosphorus, potassium, calcium, and other nutrients to microbes.

Yet nitrification may also play a negative role because nitrates not only accumulate in the soil, but may also be leached from it by virtue of their mobility, and undergo denitrification with release of gaseous forms of nitrogen

(NO, N_2O, and N_2), whereby additional losses of nitrogen from the soil occur.

Denitrification is essentially reduction of nitrate nitrogen to gaseous forms (NO, N_2O, N_2) with the result that the soil loses nitrogen, which is far from being desirable in agriculture. Responsible for denitrification is a major group of bacteria known under the generic name "denitrifiers" (*Bact. denitrificans*, *Bact. stutzeri*, *Bact. fluorescens*, *Bact. pyocyaneum*, etc.). This process is particularly intensive under anaerobic conditions in the soil, at an alkaline soil reaction, and when the soil abounds in organic matter rich in cellulose, glucose, or other carbohydrates. Denitrifying bacteria rapidly oxidize the carbohydrates to CO_2, making use of the nitrate oxygen. Nitrate reduction is an endothermic process, that is, the reaction proceeds with heat absorption. Nitrates are reduced to nitrites with the aid of the enzyme nitrate reductase, and the subsequent reduction of the nitrites is assisted by nitrite reductase. The reaction in which HNO_3 is reduced to N_2O and N_2 is as follows:

$$C_6H_{12}O_6 + 6HNO_3 \rightarrow 6CO_2 + 9H_2O + 3H_2O \ (+2289 \text{ kJ})$$

$$5C_6H_{12}O_6 + 24HNO_3 \rightarrow 30CO_2 + 42H_2O + 12N_2 \ (+2394 \text{ kJ per mole of glucose})$$

The process of respiration with nitrates permits denitrifiers to thrive under anaerobic conditions. One kg of soil containing a million *Bact. stutzeri* per gram may release 0.5 mg of nitrogen a day.

It is now known for a fact that the reduction of nitrates by denitrifying bacteria involves a few intermediate steps:

$$\underset{\text{nitrate}}{HNO_3} \rightarrow \underset{\text{nitrite}}{HNO_2} \rightarrow \underset{\text{hyponitrite}}{(HNO)_2} \rightarrow \underset{\text{nitrogen monoxide}}{N_2O} \rightarrow \underset{\text{molecular nitrogen}}{N_2}$$

Molecular nitrogen (dinitrogen) and nitrogen monoxide are the main gaseous products of biological denitrification whose volatilization accounts for nitrogen losses from the soil.

Experiments have shown that denitrification occurs extensively in soils. It takes place not only at a high moisture content and poor aeration of the soil, but also under normal moisture and aeration conditions (if the soil con-

tains nitrates and readily decomposing organic substances). Aerobiosis is never complete in soils because, even with a good structure and at an optimal moisture content, aeration may be insufficient inside soil microaggregates where favourable conditions are created for denitrification. There is a close relationship between denitrification and nitrification. Intensive formation of nitrates in aerobic soil microzones causes their depletion in oxygen; as a consequence of rapid oxygen consumption and CO_2 release by microorganisms, they become anaerobic, and appropriate conditions for denitrification are created.

Apart from biological denitrification, gaseous nitrogen losses from the soil are also due to indirect denitrification, or chemodenitrification, that is, reduction of nitrites during nitrification and biological denitrification as a result of some chemical reactions.

Microorganisms take an indirect part in chemodenitrification. Their involvement is confined to decomposition of the organic nitrogenous matter to amino acids, ammonia, and nitrous acid. As they react with one another, their nitrogen is reduced to dinitrogen:

$$\underset{\text{amino acid}}{R-NH_2} + HNO_2 = \underset{\text{hydroxy acid}}{R-CH_2COOH} + H_2O + \uparrow N_2$$

$$NH_3 + HNO_2 \rightarrow NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Dinitrogen also results from a reaction between such intermediate products of oxidation during nitrification as hydroxylamine and nitrous acid:

$$3NH_2OH + HNO_2 \rightarrow 5H_2O + 2N_2$$

The reduction of nitrates to NO, N_2O, and N_2 is also possible through their reaction with the organic matter of the soil, retaining its phenol and quinone groups even in reactions with the ions of some heavy metals (Mn^{2+}, Fe^{2+}).

Besides, nitrous acid is extremely unstable, easily degrading at an acidic reaction ($pH < 5$) into nitric acid and nitrous oxide (NO) which may then volatilize from the soil:

$$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O$$

The mineralization of organic nitrogenous matter in the soil and also nitrification and denitrification are accompanied by secondary synthetic processes in which inorganic nitrogenous compounds again turn to the unavailable organic form. These immobilization processes are of biological nature. Microorganisms build the protein of their bodies using carbohydrates and nitrogen. As nitrogenous food, they need primarily the inorganic compounds of soil-derived nitrogen (or nitrogen from fertilizers), which they convert into the protein of microbial cell plasma.

As a result of biological synthesis in the soil, nitrogen is not lost as in the case of nitrate leaching or denitrification; it merely passes into complex unavailable organic substances. After microorganisms die away and decompose, the protein nitrogen of their bodies is again partially released in an inorganic form (NH_3), the rest being incorporated into the humic substances forming in the soil during humification of the microbial protein and becoming unavailable for a longer period of time. Nitrogen mobilization and immobilization are concurrent processes, their rates and the ratio between them determining to a great extent the nitrogen regime of the soil and nitrogen nutrition conditions.

5.3 Nitrogen Cycle in Agriculture

The overall nitrogen reserves in the soil, to say nothing of the content of inorganic nitrogenous compounds in it, are constantly changing by virtue of nitrogen expenditure, on the one hand, and its replenishment, on the other.

Nitrogen in the soil is expended through uptake by plants and yield removal, and also through unproductive losses due to erosion, leaching, and denitrification.

In the case of water and wind erosion, soil particles are entrained along with the humic substances of the soil, whereby the soil is impoverished of humus and total nitrogen. Lost through erosion are mainly unavailable organic compounds of nitrogen (humic substances, etc.). The amount of inorganic forms of nitrogen in the soil decreases as a result of their immobilization, that is, conversion of NH_4^+ and NO_3^- into an organic form (protein of microorganism bodies). The maximum irrecoverable losses of available nitrogen

from the soil are due to leaching of nitrates and their breakdown by way of denitrification.

The leaching of nitrates from the soil by precipitations and drainage water is a common phenomenon. Nitrate nitrogen (NO_3^-) does not form any sparingly soluble salts in the soil, nor is it adsorbed by negatively charged soil colloids, which is why nitrates stay predominantly in the soil solution. Being thus highly mobile, nitrates easily migrate through the soil, both vertically towards the groundwater with the downward water flow and horizontally with the surface and subsurface runoff, especially in early spring and autumn. The nitrate leaching rates depend on the weather conditions, tillage system, and on whether the field is fallow or not. In humid regions, nitrate losses from fallow fields are substantial. But if a field is covered by vegetation, root absorption and sodding of the soil prevent nitrates from being leached out. Therefore, leaching of nitrates from the soil is insignificant during the vegetation period, occurring primarily in spring and in autumn in the absence of vegetative cover.

If watering is done properly on irrigated lands, when soil and subsoil waters do not merge, nitrogen loss due to leaching may be avoided. The nitrates driven down by irrigation water ascend again as the water evaporates. Soil texture becomes very important for nitrate migration. Sandy soils are washed more easily and lose more nitrates. The more compact loamy soils, particularly those rich in organic matter, are better adapted to imbibe and retain water and, hence, the nitrate nitrogen dissolved in it.

The leaching of nitrates from such soils covered by vegetation is usually insignificant, not exceeding 3 to 5 kg $N—NO_3$ per hectare. However, light soils, especially those without vegetative cover, may lose nitrogen due to nitrate leaching to a great extent (20-30 kg/ha and even more).

Another negative result of nitrate leaching is contamination of rivers and lakes.

Yet the major losses of nitrogen from the soil occur in the gaseous form as a result of denitrification. Denitrification involves both the nitrates forming in the soil and the nitrogen of the applied fertilizers after their nitrification.

Under certain conditions, the unproductive losses of nitrogen through nitrate leaching and denitrification may reach inordinate proportions. Therefore, if in virgin lands total nitrogen may be retained and even accumulated through biological fixation, arable soils tend to gradually lose it. This is not so much due to leaching of inorganic compounds of nitrogen and denitrification as to its removal with yields of farm crops.

At present, only about 20 per cent of the nitrogen removed with yields of all crops are restored in the USSR by soil manuring. Therefore, after years of cultivation without replenishing the reserves of nitrogen from other sources, its total content in the soil decreases with soil fertility.

To avoid nitrogen depletion and ensure high, stable yields of farm crops, care must always be taken to replenish nitrogen reserves in the soil. The atmosphere is a natural source of nitrogen. The air column above every hectare of the Earth's surface contains about 80 thousand tons of nitrogen. However, atmospheric molecular nitrogen is not available to most plants (with the exception of legumes). Under natural conditions, fixation of the atmospheric molecular nitrogen and replenishment of its reserves in the soil proceed in two ways. A small amount of fixed nitrogen (up to 3-5 kg/ha each year) is formed in the atmosphere itself by lightning discharges and finds its way into the soil with precipitations, in the form of ammonia and nitrates. Of particular importance is fixation of atmospheric nitrogen by nitrogen-fixing microorganisms living freely in the soil, especially nodule bacteria living in symbiosis with leguminous plants (biological synthesis of nitrogen). The free-living nitrogen-fixing microorganisms (anaerobic, such as *Clostridium pasteurianum*, and aerobic, such as *Azotobacter chroococoaceum* and others) are capable, if the conditions are right, of assimilating up to 5-10 kg/ha of nitrogen. The factors that restrict the vital activity of microbes, such as azotobacter, may include deficiency of available organic substances, phosphorus and calcium, acidic pH, low temperature, lack or excess of moisture in the soil.

Much larger amounts of atmospheric nitrogen are taken up by nodule bacteria (*Rhizobium* or *Bacterium radicicola*) living symbiotically with legumes. Under favourable living

conditions for nodule bacteria, legumes accumulate 100 to 200 kg/ha of nitrogen, and even more, throughout the vegetation period if their yields are high. The actual quantity of accumulated nitrogen depends on the leguminous crop, its yielding capacity, and soil properties.

Nodule bacteria thrive in soils with a neutral or weakly acidic reaction (pH 6.0-7.0). Liming of acid soils promotes proliferation of nodule bacteria, improves their living conditions and activity.

The activity of nodule bacteria is to a large degree dependent on the availability of nutrients in the soil. Adequate supply of organic matter, mobile phosphorus, potassium, and micronutrients (molybdenum and boron) enhances nodulation and bacterial activity. Large amounts of inorganic forms of nitrogen in the soil, on the contrary, inhibit fixation of molecular nitrogen by leguminous plants. When legumes receive too much nitrogen, nodules develop late and in smaller numbers. In this case, the importance of leguminous crops as nitrogen accumulators is less pronounced.

The activity of nodule bacteria increases with growth and development of the legume, reaching its maximum by the flowering stage. The degree of nitrogen fixation is dependent on the size of nodules to a greater extent than on the plant age. By autumn, at the end of the vegetation period, the population of bacteria in nodules is on the wane, the nodules gradually die away, and the bacteria again find themselves in the soil.

The rate of nitrogen accumulation depends on the legume species. For example, clover may accumulate 150 to 160 kg of nitrogen per hectare, lupine 160 to 170 kg, alfalfa 250 to 300 kg, soybean 100 kg, vetch, kidney bean, and pea 70 to 80 kg per hectare. About one third of the nitrogen fixed by legumes is found in root and afterharvesting residues and, after their mineralization, may be used by other plants following the legumes in crop rotation.

On the average, root and afterharvesting residues contain 10 to 15 kg of nitrogen per ton of leguminous grass hay (containing 25 to 30 kg of nitrogen), the same amount eventually getting into the soil. Hence, the contribution of biological nitrogen to the nitrogen balance is determined by the

area occupied by legumes and their yield, the latter determining the amount of nitrogen remaining in the soil with root and afterharvesting residues.

For example, if the area occupied by leguminous grasses constitutes ten per cent of the total arable area of a farm and the yield of hay is 4 t/ha, the annual supply of the soil with nitrogen, per hectare of the area sown with legumes, is 40 to 60 kg, or only 4 to 6 kg, on the average, per hectare of the entire arable area.

Leguminous crops occupy relatively small areas, and their planting in crop rotation cannot be extended without limit. The amount of biologically fixed nitrogen is not sufficient for a marked increase in all crop yields; it is far from compensating for the removal of nitrogen with yields and its losses due to leaching and denitrification. Therefore, meaningful increases in crop yields are possible only when cultivation of leguminous plants is combined with full utilization of manure and wide application of nitrogen fertilizers produced by synthesis from atmospheric nitrogen at chemical plants.

5.4 Production of Nitrogen Fertilizers and Their Application

Industrial production of nitrogen fertilizers is based on synthesizing ammonia from molecular nitrogen and hydrogen. Nitrogen is obtained by passing air through a coke oven, while the source of hydrogen is, primarily, natural and, partially, coke-oven gases rich in methane (CH_4), the latter gases containing 50% H_2.

Purified gaseous nitrogen and hydrogen (one volume of N_2 and three volumes of H_2) are gradually compressed under high pressure, then fed into a catalyst furnace. At temperatures ranging from 400 to 500 °C and a high pressure, nitrogen and hydrogen react in the presence of a catalyst to yield gaseous ammonia which is liquefied by cooling:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

Synthetic ammonia is used in the production of ammonium salts and nitric acid by oxidizing NH_3 with oxygen:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$2NO_2 + H_2O = HNO_3 + HNO_2$$
$$3NO_2 + H_2O = 2HNO_3 + NO$$

Nitric acid goes into production of nitrate and ammonium-nitrate fertilizers.

Synthetic ammonia and nitric acid are the basic products of the nitrogen fertilizer industry.

Currently, the following nitrogen fertilizers are produced:

nitrate fertilizers—sodium and calcium nitrates;

ammonium and ammonia fertilizers—ammonium sulphate, ammonium carbonates, anhydrous ammonia, and aqua ammonia (ammonium hydroxide);

ammonium-nitrate fertilizers—ammonium nitrate, calcium carbonate-ammonium nitrate, ammoniter, and liquid ammoniates;

amide fertilizers—urea and calcium cyanamide.

The development and improvement of commercial ammonia synthesis from atmospheric nitrogen, yielding cheaper nitrogen fertilizers, as well as the paramount importance of these fertilizers in increasing crop yields, have led to rapid expansion of their production and application.

The worldwide consumption of nitrogen fertilizers in 1957-58 was 7.9 million tons in terms of nitrogen, and in 1978-79 it became as high as 51.4 million tons, that is, over the past twenty years it has increased seven-fold. The production of nitrogen fertilizers in recent years has been increasing at a quicker pace than that of phosphorus and potassium fertilizers. The share of nitrogen in worldwide production of inorganic fertilizers has been steadily increasing. The ratio between N, P_2O_5, and K_2O has been changing in favour of nitrogen.

In 1978-79, the ratio between N, P_2O_5, and K_2O in the use of fertilizers around the world was 1:0.57:0.53; that is, almost as much nitrogen fertilizer has been used as phosphorus and potassium ones combined. In spite of the fact that the consumption of nitrogen in all countries has reached an extremely high level (more than 50 million tons at present),

a hectare of arable area or total farmland still receives small amounts of nitrogen on the average, i.e. 30 and 10 kg, respectively.

In this country, farms received 370 thousand tons of nitrogen fertilizers (in terms of nitrogen) in 1950, 770 thousand tons in 1960, 4605 thousand tons in 1970, and 6780 thousand tons in 1975, that is, their consumption increased 18-fold over 25 years. By 1985, farms will have received up to 11.3 million tons of nitrogen fertilizers (in terms of nitrogen), their application rate increasing to an average of 48 kg per hectare of arable land. This will permit using nitrogen fertilizers not only in the cultivation of industrial crops, but also to cover large areas occupied by grain and fodder crops. The sharp increases in the production and application of nitrogen crops go hand in hand with their diversification and improvements of their quality.

In 1960, ammonium nitrate accounted for 73 per cent of all nitrogen fertilizers, 18 per cent being represented by ammonium sulphate, and 9 per cent by the rest.

In the subsequent years, the share of ammonium sulphate and ammonium nitrate has gone down, while that of urea and compound fertilizers has gone up. In 1980, ammonium nitrate (mostly granulated) remained the major nitrogen fertilizer, yet its share in the overall production of nitrogen fertilizers decreased to 39 per cent. At the same time, sizable increases have been observed in the case of urea (up to 26%), liquid ammonia and nitrogen in compound fertilizers (29%). Ammonium sulphate and ammoniter account only for 6 per cent of the total nitrogen fertilizer production, sodium and calcium nitrates accounting for less than 0.2 per cent. Thus, high-analysis forms, such as ammonium nitrate, urea, and compound fertilizers, have been steadily gaining in importance among nitrogen fertilizers, while low-analysis ones, such as ammonium sulphate, calcium and sodium nitrates, have been becoming less important.

5.5 Nitrate Fertilizers

This category of fertilizers includes such salts as $NaNO_3$ and $Ca(NO_3)_2$. Naturally occurring chile saltpetre had long remained the only fertilizer of this group. Once the atmo-

spheric nitrogen fixation process was invented, synthetic saltpetre became available. At present, nitric acid for nitrate fertilizers is produced by oxidation of synthetic ammonia. In the USSR, nitrates are among the least commonly used nitrogen fertilizers. However, elucidation of their properties, transformations in the soil, and application are also important for gaining a better insight into other nitrogen fertilizers, including such widely used ones as ammonium nitrate and urea.

Sodium nitrate (sodium saltpetre), $NaNO_3$, contains 15-16% nitrogen and 26% sodium. It is derived in the production of nitric acid from ammonia by way of alkaline absorption of nitrogen oxides. The nitrous gases NO and NO_2, unabsorbed by water in oxidation towers, are passed through absorption towers refluxed with a soda or NaOH solution. The reaction that takes place yields a mixture of sodium nitrate and nitrite:

$$Na_2CO_3 + 2NO_2 = NaNO_3 + NaNO_2 + CO_2$$

To convert the nitrite into nitrate, the mixture is acidulated with weak nitric acid:

$$3NaNO_2 + 2HNO_3 = 3NaNO_3 + 2NO + H_2O$$

NO is returned to the oxidation towers to be oxidized to NO_2. The treated with nitric acid solution is neutralized, then concentrated by evaporation, and the precipitated $NaNO_3$ is separated from the mother liquor by centrifugation. The result is finely crystalline white or greyish sodium nitrate, which is readily soluble in water. It has pronounced hygroscopic properties and, when the humidity is high, recrystallizes into larger crystals. When stored dry under appropriate conditions, sodium nitrate remains friable and lends itself easily to placing into the soil.

Calcium nitrate (calcium saltpetre), $Ca(NO_3)_2$, contains 13-15% nitrogen. It is a product of neutralization of 40-48% nitric acid with chalk or lime:

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2$$

The nitric acid necessary for production of calcium nitrate is obtained by oxidizing ammonia.

Calcium nitrate is highly hygroscopic. At normal temperature, it readily absorbs water and becomes a hydrate.

The most stable at normal temperature is the tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$ (14.86% N).

Because of its high hygroscopicity, calcium nitrate must be transported and stored in waterproof bags impregnated with a special compound. To reduce its hygroscopicity, crystalline sodium nitrate is mixed with hydrophobic additives taken in an amount of 0.5 per cent by weight of the salt (e.g. paraffin flux). In order to improve the physical properties of the product, 4-7% ammonium nitrate is added to its concentrated solution during processing. The low nitrogen content in $Ca(NO_3)_2$ renders it uneconomical for long-distance transportation.

Calcium nitrate was the first synthetic nitrogen fertilizer. It started being produced on a commercial scale in Norway, hence its former name "Norwegian saltpetre".

Interaction of Sodium and Calcium Nitrates with the Soil. Rapidly dissolving in the soil solution, nitrates enter into exchange reactions with the absorbing complex of the soil:

$$(soil)\begin{matrix}Ca\\Ca\end{matrix} + 2NaNO_3 \rightarrow (soil)\begin{matrix}Na\\Na\\Ca\end{matrix} + Ca(NO_3)_2$$

$$(soil)\begin{matrix}H\\H\end{matrix} + Ca(NO_3)_2 \rightarrow (soil)\begin{matrix}Ca\\Ca\end{matrix} + 2HNO_3$$

The Na^+ and Ca^{2+} cations are adsorbed in the soil, while the NO_3^- anion forms soluble $Ca(NO_3)_2$ salt with the Ca^{2+} cation displaced from the absorbing complex or nitric acid with the H^+ ion.

Nitrate nitrogen does not undergo physicochemical and chemical absorption in soils. Nitrates remain highly mobile in the soil and may be leached out in easily drained soils in a humid climate or under ample irrigation. This must be taken into account in selecting the nitrate fertilizer application time. In areas with humid climate, ammonia rather than nitrate fertilizers should preferably be applied. Sodium and calcium nitrates are preferable in spring when applied during preplanting cultivation and while dressing plants during their vegetation. Sodium and calcium nitrates are physiologically alkaline fertilizers in view of the fact that plants take up more nitrogen than sodium

and calcium. Sodium and calcium will partially remain in the soil, whereby it will be alkalified. As a result, long-term application of sodium and calcium nitrates to acidic soddy podsolic soils produces a neutralizing effect.

Systematic application of nitrates, especially to soils with a low buffering capacity, perceptibly reduces their acidity.

This is illustrated by the results of a perennial experiment at the Lubertsy experimental field, carried out on soddy podsolic sandy loam. Application of sodium nitrate over a period of 18 years has reduced the exchange and hydrolytic acidities of the soil, as compared to the control plot and, particularly, to physiologically acidic ammonium sulphate, has increased the content of total exchangeable bases by a factor of 1.7, and has brought up the degree of base saturation (by 24.7% on the control plot and by 42.2% in the case of $NaNO_3$).

Application of Sodium and Calcium Nitrates. Nitrates may be applied to various soils occupied by any farm crop. Some crops (especially sugar beet and other root crops) respond better to sodium-containing nitrogen fertilizers. The higher effectiveness of $NaNO_3$ in the case of these crops stems from the positive effect of sodium on the efflux of carbohydrates from leaves into roots, which results not only in much higher yields, but also in better crop quality. On soddy podsolic soils, nitrates are more effective than physiologically acidic ammonia fertilizers. On chernozems, however, they lose this advantage, particularly for grain crops.

Sodium and calcium nitrates are used for preseeding application, drilling, and dressing of winter and row crops. Preference over other nitrogen fertilizers is usually given to sodium nitrate placed in rows seeded with sugar beet and other root crops. Calcium nitrate is not suitable for row placing because of its high hygroscopicity.

The most effective fertilizer in soddy podsolic soils is calcium nitrate. When applied systematically, it enriches the absorbing complex of the soil with calcium and leads to accumulation of calcium bicarbonate in the soil solution, thereby reducing soil acidity and improving its physical properties. As far as most crops grown on chernozems are concerned, it is equivalent to sodium nitrate and is inferior

to the latter only in the case of sugar beet, fodder, and table roots. Sodium nitrate is not recommended for application to saline and alkaline soils.

Nitrates are less effective than ammonia fertilizers when applied in irrigated areas where rice, cotton, and other crops are cultivated.

5.6 Ammonia Fertilizers

These are easier to produce than nitrate fertilizers. Their production does not require oxidation of ammonia to nitric acid. Before ammonia synthesis was invented and improved, the raw material for ammonium sulphate production was coal which contains 0.5-1.5% N. When coal is carbonized, nitrogen is partially released in the form of ammonia which is trapped in the coke-oven gas scrubber. For complete removal of NH_3, milk of lime (suspension of $Ca(OH)_2$ in water) is added to the ammonia dissolved in boiling water, which is then bound with sulphuric acid.

Ammonia fertilizers include ammonium sulphate, ammonium chloride, ammonium carbonates, and liquid ammonia fertilizers.

5.6.1 Solid Ammonia Fertilizers

Ammonium sulphate, $(NH_4)_2SO_4$, contains 20.5-21% nitrogen. Ammonium sulphate accounts for 25 per cent of all nitrogen fertilizers produced worldwide (less than 6 per cent in the Soviet Union). It is a product of neutralization of sulphuric acid with the ammonia released from coke-oven gases during carbonization of coal (coke-oven ammonium sulphate) or absorption of gaseous synthetic ammonia by sulphuric acid (synthetic ammonium sulphate):

$$H_2SO_4 + NH_3 = (NH_4)_2SO_4$$

The $(NH_4)_2SO_4$ precipitating in the saturated solution is separated by centrifugation and dried. Because of the low cost of the ammonia derived from coke-oven gases, coke-oven ammonium sulphate is cheaper than the synthetic one.

In the USSR, only coke-oven ammonium sulphate is produced. In the production of ammonium sulphate, sulphuric

acid may be replaced by less expensive natural minerals, such as gypsum ($CaSO_4 \cdot 2H_2O$) and mirabilite, or Glauber salt (crystal hydrate $Na_2SO_4 \cdot 10H_2O$). If sodium sulphate is used to bind ammonia, in addition to ammonium sulphate the reaction will yield soda which is also a valuable chemical:

$$Na_2SO_4 + 2NH_3 + 2CO_2 + 2H_2O = (NH_4)_2SO_4 + 2NaHCO_3$$

Ammonium sulphate is easily soluble in water. When dry, it exhibits good physical properties: it has no tendency to cake in storage and is easily spread by a dry-fertilizer broadcaster. Its hygroscopicity is low. The fertilizer does not deliquesce in air and remains friable.

Ammonium sulphate is essentially a crystalline salt of different colours. Synthetic ammonium sulphate is white and contains 20.5-21% nitrogen, 0.2-0.3% moisture, and 0.025-0.05% free sulphuric acid which renders the fertilizer weakly acidic. Coke-oven ammonium sulphate also contains a small amount of organic impurities, such as resin acids, phenol, and a little (not more than 0.1%) ammonium thiocyanate (NH_4SCN). The latter is toxic for plants and may even harm them if present in increased amounts, especially on soils with a low humus and calcium content.

Organic impurities are responsible for the grey and sometimes bluish or reddish colour of coke-oven ammonium sulphate. It contains 23-24% sulphur and is a major source of this nutrient for plants.

Ammonium-sodium sulphate, $(NH_4)_2SO_4 \cdot NaSO_4$, contains at least 16% nitrogen and up to 2.5% organic impurities. This fertilizer is a by-product of caprolactam processing. It is a yellowish crystalline salt. The Na_2SO_4 content is 20 to 25 per cent, and that of Na_2O is about 9 per cent. By virtue of its sodium content, this is a good fertilizer for sugar beet grown on chernozems and limed soddy podsolic soils, as well as plants belonging to the cruciferae family, responsive to sulphur and sodium.

Ammonium chloride, NH_4Cl, contains 24-25% nitrogen. It is a by-product of soda processing:

$$NH_3 + CO_2 + H_2O + NaCl = NaHCO_3 + NH_4Cl$$

Ammonium chloride is water-soluble, displays good physical properties, has low hygroscopicity, and does not cake

in storage. It also exhibits pronounced physiological acidity and contains a lot of chlorine (66.6%) which may lower the quality of such crops as potato, tobacco, and grape. On soddy podsolic soils, chlorine also adversely affects onion, cabbage, hemp, and flax. In the case of grain crops, when applied at normal rates, ammonium chloride is sometimes as good as ammonium sulphate.

Ammonium chloride should not be applied at increased rates to fertilize crops sensitive to chlorine. It must be incorporated well in advance, in autumn, in which case chloride ions are not adsorbed in the soil and are easily leached from the root layer by precipitation.

Ammonium carbonate, $(NH_4)_2CO_3$, is obtained through saturation of aqua ammonia with carbon dioxide with subsequent distillation at 70 to 80 °C or as a result of a reaction between gaseous ammonia and carbon dioxide in the presence of water vapours. Ammonium carbonate is extremely unstable, degrades in air, releasing ammonia and converting into ammonium bicarbonate. The commercial product contains 21-24% nitrogen and is a mixture of ammonium carbonate, ammonium bicarbonate, and ammonium carbamate.

Ammonium bicarbonate, NH_4HCO_3, is produced through adsorption of gaseous ammonia and carbon dioxide by an ammonium carbonate solution

$$\underset{\text{solution}}{(NH_4)_2CO_3} + H_2O + \underset{\text{gas}}{CO_2} = 2NH_4HCO_3$$

White crystalline ammonium bicarbonate precipitates, and that remaining in solution is saturated with gaseous ammonia:

$$NH_4HCO_3 + NH_3 = (NH_4)_2CO_3$$

The ammonium carbonate forming in solution is reused in ammonium bicarbonate production. The fertilizer contains about 17% nitrogen. In its effect on plants it is similar to ammonium nitrate. It is more stable than ammonium carbonate, although ammonia losses are possible in storage, transportation, and application. After broadcasting, ammonium bicarbonate must be immediately incorporated into the soil.

Interaction of Ammonium Sulphate with the Soil. The incorporated ammonium sulphate, $(NH_4)_2SO_4$, quickly dissolves and immediately enters into exchange reactions with cations of the solid phase of the soil. Most of the NH_4^+ cations from the fertilizer dissolved in the soil enter the absorbing complex of the soil, while the soil solution receives an equivalent amount of other cations:

$$(\text{soil})\begin{matrix}\text{Ca}\\\text{Ca}\end{matrix} + (NH_4)_2SO_4 = (\text{soil})\begin{matrix}\text{NH}_4\\\text{NH}_4\end{matrix} + CaSO_4$$

The absorbed ammonium is readily taken up by plants. At the same time, being in the absorbed state, the ammonium ion becomes less mobile. As a consequence, the possibility of nitrogen leaching from the ammonium sulphate placed in a water-logged soil is ruled out.

However, the low mobility of ammonium in the soil may also produce a negative effect: ammonia nitrogen is concentrated in the soil locally, at spots where the fertilizer has been applied. Therefore, when ammonium sulphate is used for dressing or drilling at seeding, the uptake of nitrogen by plants may be inhibited. At the beginning of growth and development, plants do not yet have an extensive root system and the root does not always reach the zone supplied with nitrogen.

Ammonia fertilizers are also less suitable for drilling since intensive influx of ammonia nitrogen into the young sprouts may harm them because of the toxicity of excess ammonia.

As a result of nitrification, nitrogen of ammonium sulphate (and also ammonium chloride) converts into the nitrate form. Nitrate nitrogen is not adsorbed by soil colloids, does not form insoluble compounds, and remains in the soil solution so that intimate contact with the active root system of plants is ensured. In the course of nitrification of ammonia nitrogen, the difference in mobility between the nitrogens of nitrate and ammonia fertilizers disappears, although within few days after application this difference is pronounced. Therefore, the nitrate form of nitrogen is preferable over the ammonia one when it comes to drilling and dressing. The conversion of ammonia nitrogen to the nitrate form proceeds at different rates depending on temperature,

moisture content, aeration, and soil reaction. The process of biological oxidation of the nitrogen in the incorporated ammonium sulphate (nitrification) yields nitric acid and releases sulphuric acid:

$$(NH_4)_2SO_4 + 4O_2 = 2HNO_3 + H_2SO_4 + 2H_2O$$

These acids are neutralized in the soil as they enter into reactions with the bicarbonates of the soil solution and the cations of the absorbing complex:

$$2HNO_3 + Ca(HCO_3)_2 = Ca(NO_3)_2 + 2H_2CO_3$$

$$H_2SO_4 + Ca(HCO_3)_2 = CaSO_4 + 2H_2CO_3$$

$$(soil)\begin{matrix}Ca\\Ca\end{matrix} + 2HNO_3 = (soil)\begin{matrix}Ca\\H\\H\end{matrix} + Ca(NO_3)_2$$

$$(soil)\begin{matrix}Ca\\Ca\end{matrix} + H_2SO_4 = (soil)\begin{matrix}Ca\\H\\H\end{matrix} + CaSO_4$$

The neutralization of inorganic acids is accompanied by breakdown of the bicarbonates of the soil solution and displacement of bases from the absorbing complex by hydrogen. This lowers somewhat the buffering capacity of the soil and increases its acidity.

The change in soil reaction due to application of ammonium sulphate and ammonium chloride is also caused by their physiological acidity. Plants take up the cation from $(NH_4)_2SO_4$ and NH_4Cl more readily than the anion because they need nitrogen more than sulphur and chlorine. Acid residues are accumulated in the soil and acidify it.

Soddy podsolic soils with a small amount of calcium and organic matter are acidified more rapidly and considerably than chernozems rich in organic matter and calcium, to say nothing of sierozems containing a lot of calcium carbonate. When applied once, ammonium sulphate may produce no effect on the reaction even of soddy podsolic soil. Systematic application of ammonium sulphate leads to marked acidification of this soil (Table 5.3).

On plots fertilized with ammonium sulphate, soil acidity and the mobile aluminium content increased drastically, while the degree of base saturation decreased.

Long-term application of ammonium sulphate influences the properties of soddy podsolic soils and chernozems with a

Table 5.3. Effect of Ammonium Nitrate and Ammonium Sulphate on Soil Acidity and Composition of the Absorbing Complex (results of 16-year-long field experiment)

Experimental conditions	Exchange acidity	Hydrolytic acidity (Hr)	Total exchangeable bases (S)	Exchange capacity ($S + H$)	Degree of base saturation (V, %)	Mobile Al (mg per 100 g of soil)
	meq/100 g of soil					
No fertilizer	1.1	4.0	6.5	10.5	61.8	10.0
NH_4NO_3	1.0	4.1	6.7	10.8	61.6	8.7
$(NH_4)_2SO_4$	1.8	5.4	6.2	11.6	53.5	16.4

pronounced buffering capacity. For example, according to the results of experiments at the Mironovka station, application of this fertilizer to chernozem over a period of 14 years has led to drastic changes in soil reaction. In experiments without fertilizer application, the pH of the salt extract was 6.0, in the case of ammonium sulphate, the pH was 4.9; the exchange acidity of the soil increased 1.5-fold, while the hydrolytic one, almost 2.5-fold, as compared to the control.

However, even after such a prolonged application of the physiologically acidic ammonium sulphate to this soil, no negative effect on crop yields has been observed. As regards humus-rich chernozems characterized by high natural fertility and buffering capacity, weak acidification may even be beneficial to some extent.

Nor have any unfavourable changes been observed when ammonium sulphate was applied even over a longer period of time to chestnut soils and sierozems of Central Asia because the acidic residues of the fertilizer are fully neutralized with calcium and form bicarbonates. Therefore, there is no reason to fear acidification of calcareous soils to which physiologically acidic fertilizers are applied.

Ways to Enhance the Effectiveness of Ammonia Fertilizers. Ammonium sulphate (just as ammonium chloride) is applied preferably before seeding as a basal fertilizer, and it can be applied not only in spring, but also well in advance, in autumn, without any danger of nitrogen leaching.

The effect of ammonium sulphate depends primarily on soil acidity and buffering capacity as well as the biological characteristics of farm crops.

Systematic application of ammonium sulphate to soddy podsolic soils having a low buffering capacity makes them more acidic with the result that the plant growth conditions deteriorate and the fertilizer becomes less effective. To enhance the effect of ammonium sulphate on crop yields, acidic soddy podsolic soils must be limed, while unlimed soils should be neutralized with crushed chalk, limestone, and dolomite prior to application of this fertilizer. To neutralize the physiological acidity of a centner of ammonium sulphate takes 1.3 centners of lime carbonate ($CaCO_3$). While improving the buffering capacity of the soil, systematic manuring also mitigates the deleterious effect of this fertilizer on soil properties and plays a major role in improving its effectiveness. When applied to soddy podsolic soils, ammonium sulphate is highly effective when it is combined with alkaline or neutral forms of phosphorus fertilizers (Thomas slag, ground phosphate rock).

The effectiveness of ground phosphate rock on soddy podsolic soils is enhanced by high rates of ammonium sulphate. Its physiological acidity promotes dissolution of tricalcium phosphate to available orthophosphates. Here, ammonium sulphate also produces an indirect effect on plants by improving their nutrition not only with nitrogen, but also with phosphorus. The presence of calcium in the soil solution is important both for neutralization of the residual acidity of the nitrogen fertilizer and for maintaining the physiological equilibrium of the soil solution.

On acid soils of the Non-Black Earth zone, ammonium sulphate often produces a weaker effect on crop yields than nitrates. On chernozems, the effectiveness of ammonia and nitrate fertilizers is equalized (Table 5.4).

Apart from soil properties, the effectiveness of ammonium sulphate is also dependent on the crop characteristics. Crops less sensitive to acidic soil reaction (oat, winter rye, flax, potatoes) will respond less strongly to the acidifying effect of ammonium sulphate. On the other hand, crops thriving on neutral or weakly acidic soils (most vegetables, sugar beet, barley, hemp, spring wheat, etc.) are the first to be

Table 5.4. Effectiveness of Nitrogen Fertilizers on Slightly Leached Loamy Chernozem (results of experiments at the Sumy station)

Experimental conditions	Barley yield (cent/ha)		Grain yield increase (%)
	grain	straw	
No fertilizer	20.0	22.5	—
$NaNO_3$	27.6	35.7	38
$(NH_4)_2SO_4$	28.3	36.0	41

Table 5.5. Crop Yields (cent/ha) **After Application of Various Nitrogen Fertilizers** (6th and 7th year after application)

Experimental conditions	Oat (grain)	Potato (tubers)	Sugar beet (roots)
No nitrogen	12.5	178.6	189.9
$(NH_4)_2SO_4$	15.2	200.8	163.2
$NaNO_3$	15.9	212.7	309.9

inhibited by systematic application of ammonium sulphate (Table 5.5).

After the exchange acidity of the soil on plots treated with ammonium sulphate had sharply increased, the yields of oat and potatoes were almost as high as in the experiment with $NaNO_3$. At the same time, the yield of sugar beet, a crop sensitive to acidification of the soil reaction, decreases perceptibly when ammonium sulphate is systematically applied. On soils saturated with bases and characterized by high neutralizing capacity, such as calcareous chernozems and sierozems, the effectiveness of ammonium sulphate, even when applied systematically, is as high as and often higher than that of nitrate fertilizers.

The advantages of one or another nitrogen fertilizer depend on crop behaviour. Potatoes are responsive to application of both ammonium sulphate and calcium or sodium nitrate. Hemp grows better when the soil is fertilized with nitrates. Rice grown on flooded paddies, where the nitri-

fication processes are heavily inhibited because of oxygen deficiency, is better adapted to ammonia nutrition. Sugar beet grown on neutral buffer soils responds similarly to ammonia and nitrate as part of the basic fertilizer. On the other hand, when nitrogen is additionally applied in the row at seeding or for dressing, nitrates, especially the sodium one, are more effective.

More suitable for dressing of winter wheat and winter rye are nitrate or ammonium-nitrate fertilizers, high yield increases being also ensured by ammonium sulphate. On irrigated lands, good results are attained by application of ammonia fertilizers.

5.6.2 Liquid Ammonia Fertilizers

Along with solid ammonia fertilizers, use is made of liquid ones, such as anhydrous or liquid ammonia and aqua ammonia (ammonium hydroxide). They are much simpler and cheaper to produce than the solid salts. The cost of liquid fertilizers, for example anhydrous ammonia, per unit nitrogen constitutes only 40 per cent of that of ammonia nitrate.

Anhydrous ammonia, NH_3, is the most concentrated dead weight-free fertilizer. It contains 82.3% nitrogen and is produced by liquefaction of gaseous ammonia under pressure. Anhydrous ammonia is a colourless mobile liquid having a density of 0.61 at 20 °C and boiling at 34 °C. At higher temperatures, it becomes gaseous at once and its volume increases. When stored in open vessels, NH_3 quickly evaporates. It is characterized by high vapour pressure (at 10 °C, the vapour pressure is 5.2 kgf/cm^2, increasing to 13.8 kgf/cm^2 at 37.8 °C). To prevent anhydrous ammonia from volatilization, it is stored and transported in special steel tanks.

When placed in the soil, anhydrous ammonia turns to gas which is adsorbed by the colloidal fraction and absorbed by soil moisture to form ammonium hydroxide. As it interacts with the soil solution anions, ammonia yields different salts and, entering into a physicochemical reaction with soil colloids, is adsorbed by the solid phase of the soil. Apart from physicochemical reactions, ammonia also undergoes nitrification. The rate and degree of ammonia

adsorption in the soil depend on the humus content in the latter, its texture and moisture content, as well as the application technique and depth. In heavy, humus-rich, properly tilled and adequately moistened soils, ammonia is adsorbed more readily than in light, humus-poor ones. In sandy and sandy loam soils, the formation of ammonium salts from ammonia and adsorption of the ammonium ion are much slower than in soils with heavy texture. This is why, in light soils, the fertilizer long remains in the form of NH_3 and tends to volatilize. The volatilization of ammonia from a moist soil is much less pronounced than from a dry one.

Aqua ammonia is essentially an aqueous solution of synthetic or coke-oven ammonia. It comes in two grades: grade one contains 20.5% nitrogen (25% caustic ammonia), while grade two contains 16.4% N (20% ammonia). Coke-oven aqua ammonia also contains hydrogen sulphide and trace amounts of phenols, thiocyanates, cyanates, and other compounds.

Aqua ammonia is characterized by a low ammonia vapour pressure (0.15 kgf/cm^2 at 40 °C in the case of 25% ammonia), does not attack ferrous metals, and freezes only at an extremely low temperature (25% ammonia freezes at —56 °C and 20% ammonia, at —33 °C). Hence, it may be stored and carried in airtight vessels made of ordinary carbon steel and designed to a low pressure (0.4 kgf/cm^2). Nitrogen in aqua ammonia takes the form of free ammonia (NH_3) and ammonium hydroxide (NH_4OH). The equilibrium ratio between NH_3 and NH_4OH in aqua ammonia, $[(NH_4^+)\cdot(OH^-)] : [NH_3\cdot H_2O] = 10^{-5}$, indicates that it contains much more ammonia than ammonium. This accounts for possible nitrogen losses during transportation, storage, and application of fertilizers due to volatilization of ammonia.

As soon as aqua ammonia is placed in the soil, ammonia is adsorbed by colloids and loses mobility. In the course of time, ammonia nitrogen is nitrified and, becoming more mobile, migrates with the soil solution. Technically, application of aqua ammonia is simpler and safer as compared to anhydrous ammonia, although it has a serious disadvantage of containing little nitrogen, which leads to greater expenditures involved in transportation, storage, and application. Therefore, using aqua ammonia is worthwhile only

at farms located near plants where this fertilizer is produced.

All liquid nitrogen fertilizers are applied using special machines that ensure their immediate incorporation to a depth of at least 10 to 12 cm in heavy soils and 14 to 18 cm in light soils. When liquid fertilizers are placed in this manner, ammonia does not volatilize from the soil. Some losses are possible only on markedly calcareous soils. Surface application of liquid nitrogen fertilizers is inadmissible because of the rapid evaporation of ammonia. Shallow placement in the dry topsoil also may lead to considerable ammonia losses, particularly in the case of light sandy and sandy loam soils. Liquid nitrogen fertilizers are applicable to all farm crops, primarily before seeding. They may be applied not only in spring prior to seeding, but also much earlier, in autumn. However, application of these fertilizers at high rates in autumn to light sandy and sandy loam soils may entail ammonia losses because not all of ammonia is adsorbed by the soil.

At a high ammonia concentration in the application zone, the vital activity of soil microflora is temporarily suppressed and nitrification is slowed down. As a result of local concentrations of ammonia nitrogen in the soil, application of liquid nitrogen fertilizers under close-growing crops with widely spaced colters (35-50 cm) may result in uneven stands. Plants closer to the application zone will be better supplied with nitrogen and develop better than those farther from the colter path. Therefore, liquid nitrogen fertilizers should be applied before planting of cereals, flax, and other narrow-row crops with the aid of machines with more closely spaced colters (20-25 cm), and the seeding should be performed at a right angle to the direction of application. When used for dressing row crops, liquid nitrogen fertilizers are placed in the middle between rows or at a distance of 15 to 20 cm from the latter so as not to damage young plants by excess ammonia concentrations; to ensure even distribution of ammonia nitrogen in the soil, the subsequent inter-row tillage is of great importance. As ammonia is being nitrified, the resulting nitrates migrate with the soil moisture, and the concentration of available nitrogen in the soil is equalized. The nitrification rate depends on soil properties (in chernozems and limed soddy podsolic soils, it is faster than in

acid podsolic soils). Synthetic aqua ammonia is nitrified at a faster rate, as compared to the coke-oven variety.

Experiments aimed at studying the effectiveness of anhydrous ammonia and aqua ammonia with respect to various crops have shown that, if properly applied (using special machinery), they are as effective, at equal rates in terms of nitrogen, as ammonium nitrate.

5.7 Ammonium-Nitrate Fertilizers

This group of fertilizers containing nitrogen in ammonium and nitrate forms includes ammonium nitrate, the most widely used nitrogen fertilizer.

Ammonium nitrate (ammonium saltpetre), NH_4NO_3, contains 34.6% nitrate and ammonia nitrogen. It is produced by neutralization of 56-60% nitric acid with gaseous ammonia:

$$\underset{\text{gas}}{HNO_3 + NH_3} = NH_4NO_3$$

To obtain the end product, the solution is evaporated to a 95-98% concentration of NH_4NO_3 which is then recrystallized and dried. The result is a white crystalline substance containing 98-99% NH_4NO_3. The impurities it contains are mainly the additives introduced into ammonium nitrate to improve its physical properties.

Ammonium nitrate is highly hygroscopic with a pronounced tendency to become damp in air and to cake. To prevent it from caking, a small amount of conditioning additives (finely ground phosphate rock or bone meal, gypsum, kaolinite, etc.) is introduced. These additives do not decompose ammonium nitrate, absorb large quantities of moisture, and are responsible for the yellowish colour of the product. Sometimes, dyes are used as additives. The physical properties of ammonium nitrate largely depend on the size and shape of the produced crystals. Currently, chemical plants produce ammonium nitrate in the form of pellets (spherical, 1-3 mm in diameter) and flakes. Granulated ammonium nitrate exhibits superior physical properties, as compared to the crystalline one, and retains good friability and drillability.

In terms of quality, ammonium nitrate must meet the following requirements: nitrogen content of at least 34.6 per cent, moisture content not exceeding 0.4 per cent, neutral or weakly acidic reaction, and content of water-insoluble impurities of not more than 0.1 per cent. The fertilizer is packaged in waterproof five-wall paper bags. It must be kept in dry storage, otherwise even pelletized nitrate is caked and, before application, has to be crushed to become friable and sifted through screens with 2- to 3-mm mesh. In order to improve the physical properties of ammonium nitrate, it is mixed, during storage, with precipitate or ground phosphate rock (for soddy podsolic soils). Immediately before application to an acid soil, ammonium nitrate may also be mixed with 30-40% calcium carbonate. This gives a mixture of low hygroscopicity, lending itself easily to broadcasting. Lime neutralizes the physiological acidity of this fertilizer.

Interaction of Ammonium Nitrate with the Soil. Ammonium nitrate is dissolved in soil moisture rapidly and completely. As has been established in physiological experiments at Pryanishnikov's laboratory, plants take up NH_4^+ cations from an ammonium nitrate solution at a faster rate than NO_3^- anions. Therefore, ammonium nitrate is classified with physiologically acidic fertilizers. However, its physiological acidity is much lower than that of ammonia fertilizers, such as ammonium sulphate. After incorporation into the soil, ammonium nitrate enters into a reaction with its absorbing complex:

$$(\text{soil})\begin{matrix}\text{Ca}\\\text{Ca}\end{matrix} + 2NH_4NO_3 = (\text{soil})\begin{matrix}\text{NH}_4\\\text{NH}_4\\\text{Ca}\end{matrix} + Ca(NO_3)_2$$

As a result of exchange adsorption, ammonium is adsorbed by soil colloids, while the NO_3^- anion forms salts with calcium, magnesium, and other ions in the soil solution.

In base-saturated soils (chernozem and sierozem), the solution is not acidified even when the fertilizer is applied systematically at high rates. Ammonium nitrate is one of the best forms of nitrogen fertilizers for these soils. If a soil is calcium-deficient (as is the case with acidic soddy podsolic soils), application of ammonium nitrate may cause slight acidification of the soil solution and, in the case of uneven

application, create high acidity spots:

$$(\text{soil})\begin{matrix}\text{H}\\\text{Ca}\end{matrix} + 3\text{NH}_4\text{NO}_3 = (\text{soil})\begin{matrix}\text{NH}_4\\\text{NH}_4\\\text{NH}_4\end{matrix} + \text{HNO}_3 + \text{Ca}(\text{NO}_3)_2$$

Local acidification of the soil solution is but temporary, the acidity disappearing as plants take up nitrate nitrogen. However, a decrease in the pH value of the soil solution may inhibit the early growth and development of the still weak plant organism as well as promote dissolution of such compounds as aluminium hydroxide which is toxic for plants. The nitrification of ammonium nitrate in soils with a low buffering capacity also causes temporary acidification of the soil:

$$2\text{NH}_4\text{NO}_3 + 4\text{O}_2 = 4\text{NHO}_3 + 2\text{H}_2\text{O}$$

The effect of ammonium nitrate on the acidity and composition of exchangeable cations in soddy podsolic loam is much less pronounced than that of ammonium sulphate. However, when it is applied over a long period of time to soddy podsolic soils with low buffering capacity and light texture, the acidification may be significant with the result that the effectiveness of ammonium nitrate, especially for crops sensitive to high acidity, decreases appreciably.

Half the nitrogen in ammonium nitrate is in the form of ammonium which is adsorbed by the soil, the other half being in the form of nitrates characterized by high mobility in the soil solution.

When ammonium nitrate is applied together with, for example, sodium nitrate at the same nitrogen rate the concentration of nitrates in the soil solution will be lower in the former case than in the latter, and the ammonia nitrogen of ammonium nitrate in the form of NH_4^+ will be rapidly adsorbed by soil colloids, which is why the danger of its leaching under conditions of ample moisture is less than in the case of sodium nitrate.

Exchangeable ammonium remains available to plants. However, under certain conditions, NH_4^+ may be adsorbed in the soil in a completely or almost non-exchangeable form which cannot be taken up by crops.

Besides, after having been incorporated into the soil, the ammonium and nitrate nitrogen of this and other fertil-

izers is taken up not only by plants, but also by microorganisms so that it partially takes the form of complex organic compounds unavailable to plants. After microorganisms die away and decompose, the nitrogen they contain is again partially liberated in an inorganic form and can be taken up by plants, the rest being converted, during degradation of the microbial protein, into humic substances and becomes unavailable for a longer period of time.

Conditions for Effective Use of Ammonium Nitrate and Its Application Techniques. Ammonium nitrate often ranks first among nitrogen fertilizers, insofar as its effectiveness is concerned. It can be used with success to fertilize all soils in the USSR for cultivation of various crops. For ammonium nitrate to be more effective when applied systematically to acidic soddy podsolic soils with a low buffering capacity, it is important that these soils be limed. The negative effect of the potential acidity of ammonium nitrate may also be obviated by neutralizing it with lime or dolomite (a centner of $CaCO_3$ per centner of the fertilizer). The effectiveness of fertilizers largely depends on their application techniques.

Distinction is made between preseeding (basal), starter (drilling), and supplemental (dressing) applications.

The fact that half the nitrogen in ammonium nitrate is in the highly mobile nitrate form, while the other half is in the less mobile ammonia form, makes it advantageous over other nitrogen fertilizers in the sense that its application techniques, rates, and times can be varied widely depending on soil properties, climatic conditions, and crops.

Ammonia nitrate is applied as a preseeding (basal) fertilizer, in the row or holes at seeding or for dressing during the vegetation period.

In a humid climate, especially on light soils where nitrate nitrogen may be leached out, ploughdown of ammonium nitrate in autumn is less effective than in spring, during preseeding cultivation. In less humid regions, it may be applied in autumn without any fear of nitrogen leaching. Ammonium nitrate is also placed at low rates (10-15 kg N) together with other fertilizers in the row when seeding sugar beet or in holes when planting potatoes, vegetables, and other crops. Ammonium nitrate is one of the best nitrogen

fertilizers for dressing winter crops in early spring. It may also be used for dressing row and vegetable crops, in which case it must be incorporated between rows to a depth of 10 to 15 cm by a cultivator-fertilizer or during the subsequent inter-row tillage.

5.8 Fertilizers Containing Nitrogen in the Amide Form

Urea (carbamide), $CO(NH_2)_2$. Synthetic urea contains 46% nitrogen, which makes it the most concentrated solid nitrogen fertilizer. The starting materials used in the production of synthetic urea are gaseous or liquid ammonia and carbon dioxide. It is yielded by a reaction between carbon dioxide and ammonia, conducted at high pressure and temperature:

$$CO_2 + 2NH_3 = CO(NH_2)_2 + H_2O$$

Urea is a white crystalline substance readily soluble in water. Its hygroscopicity at temperatures of up to 20 °C is relatively low (approaching that of ammonium sulphate) but increases perceptibly with temperature. When stored, crystalline urea may cake with detriment to its drillability. The commercial product is usually granulated, each granule ranging from 1 to 3 mm in diameter. To minimize caking, the granules are coated with a thin layer of a fatty additive. Granulated urea exhibits superior physical properties, does not cake, and retains good drillability. In the course of granulation, biuret forms in urea under the effect of temperature:

$$2CO(NH_2)_2 \rightarrow (CONH_2)_2HN + NH_3$$

When present in large amounts (exceeding 3%), biuret becomes toxic for plants, and application of urea containing more than 3% biuret immediately before seeding inhibits plant development.

Biuret completely decomposes in the soil within the first 10 to 15 days, hence, when urea is applied one or two months before seeding, it produces no harmful effect on young plants, no matter how much biuret it contains. In crystalline urea, the biuret content does not exceed 0.2 to 0.8 per cent, and currently produced granulated urea contains no more than

one per cent of this substance. When present in such a small amount, biuret does not harm sprouts irrespective of the urea application time. Granulated urea is virtually as effective as the crystalline product, whenever and however applied.

Interaction of Urea with the Soil. Urea is completely dissolved by soil moisture and rapidly ammonified by the enzyme urease released by urobacteria, being converted into ammonium carbonate:

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3$$

Under favourable conditions, in humus-rich soils, it takes two to three days for urea to be converted into ammonium carbonate, the ammonification process being slower in infertile sandy and marshy soils.

Ammonium carbonate is an unstable compound, which decomposes in air into ammonium bicarbonate and gaseous ammonia:

$$(NH_4)_2CO_3 \rightarrow NH_4HCO_3 + NH_3$$

Therefore, when urea is spread on the surface without being incorporated into the soil and in dry weather, nitrogen may be partially lost in the form of ammonia. These nitrogen losses are more pronounced from soils with a neutral and alkaline reaction. In the soil, ammonium carbonate undergoes hydrolysis to form ammonium bicarbonate and ammonium hydroxide:

$$(NH_4)_2CO_3 + H_2O = NH_4HCO_3 + NH_4OH$$

The ammonium forming when urea is placed in the soil is adsorbed by its colloidal fraction and gradually taken up by plants. It has been established that urea can be absorbed by roots and taken up by leaves without being first converted into ammonium carbonate. However, urea itself may be leached out of the soil before undergoing ammonification. During ammonification of urea, the soil may be alkalinized temporarily near the application points as a result of ammonium carbonate hydrolysis. In the course of time, ammonium is nitrified yielding nitric acid:

$$2NH_3 + 3O_2 = 2HNO_2 + 2H_2O$$

$$2HNO_2 + O_2 = 2HNO_3$$

The nitrification of ammonium carbonate proceeds much faster than that of ammonium sulphate and especially chloride. At the ammonium nitrification stage, temporary local alkalinization is superseded by acidification. However, after the nitrogen of urea has been taken up by plants, neither alkaline nor acidic residues remain in the soil. The degree of acidification of the soil per unit urea nitrogen is approximately the same as in the case of ammonium nitrate.

Application of Urea. Urea is used as a preseeding fertilizer on all soils occupied by various farm crops. Field experiments have shown that, when applied before seeding, urea is as effective, in all parts of this country and for most crops, as ammonium nitrate and, for rice and tea, as ammonium sulphate.

In areas with adequate moisture content in light soddy podsolic soils and irrigated sierozems, urea is responsible for higher increases in the yields of certain crops (potatoes, sugar beet, vegetables), as compared to ammonium nitrate. This is due to the fact that the amide nitrogen of urea is rapidly converted into ammonia nitrogen which is adsorbed by the soil and is leached downward to a lesser extent.

When used for dressing winter crops in early spring, urea is as highly effective as ammonium nitrate. It may also be used to dress row and vegetable crops with immediate incorporation into the soil. If the incorporation is delayed, nitrogen may be lost because of volatilization of the ammonia forming in the decomposition of the ammonium carbonate into which urea is converted. The latter may also be used for foliar dressing as well but, in this case, crystalline urea with a lower biuret content (0.2-0.3%) is preferable.

Unlike other forms of nitrogen fertilizers, urea does not burn leaves even when used in a high concentration (1% solution) while being fully utilized by the plants. It may be taken up by leaf cells as a whole molecule and assimilated by plants not only by way of preliminary degradation into ammonia under the effect of urease, but also through direct involvement in the cycle of transformations of nitrogenous substances, yielding diamino acids. Application of urea in the row at seeding may slow down sprouting because its degradation results in excess amounts of free ammonia in the root zone.

As a consequence of high nitrogen content in urea, it must be evenly distributed when placed in the soil. To this end, urea is intimately mixed with other fertilizers prior to application. When urea is used alone, it is mixed with dry sand.

Owing to its outstanding physical properties and high nitrogen content, urea is considered to be one of the best nitrogen fertilizers, and its production has been steadily increasing.

Calcium cyanamide, $CaCN_2$, contains 20-22% nitrogen. The commercial product includes 58-60% $CaCN_2$, 20-28% CaO, 9-12% carbon, and trace amounts of silicic acid, iron oxide, aluminium, and calcium carbide.

Calcium cyanamide is a light, fine black or dark grey powder dusting considerably when handled and broadcast. When it gets in the eyes and respiratory organs, calcium cyanamide causes inflammation of the mucous membrane and erosion of the skin, which makes it necessary to wear goggles and gloves for protection.

When in the soil, calcium cyanamide is hydrolyzed and interacts with the soil absorbing complex:

$$2CaCN_2 + 2H_2O = Ca(CNNH)_2 + Ca(OH)_2$$

$$(soil)\begin{matrix}H\\H\end{matrix} + Ca(CNNH)_2 = (soil)Ca + 2H_2CN_2$$

The resulting cyanamide (H_2CN_2) is toxic for plants but is soon converted into urea:

$$H_2CN_2 + H_2O = CO(NH_2)_2$$

Catalyzed by urease, urea is converted into ammonium carbonate which yields nitric acid when nitrified.

Calcium cyanamide is an alkaline fertilizer in view of its high content of CaO which alkalizes the soil. Systematic application of calcium cyanamide to acidic soddy podsolic soils substantially improves their properties by virtue of partial neutralization of the acidity and enrichment with calcium. In order to preclude the harmful effect of the undecomposed cyanamide in the soil on germinating seeds or young sprouts, it is to be applied in advance: seven to ten days before seeding in spring or during ploughing in autumn. Calcium cyanamide is produced in small quantities because its use is limited, being restricted primarily to preharvesting defoliation of cotton and other crops.

5.9 Slow-Acting Fertilizers

All commercially produced nitrogen fertilizers (except for $CaCN_2$) are readily soluble in water. The high solubility and mobility of nitrogen fertilizers in the soil are not always of advantage. When applied at high rates, they tend to accumulate in excessively harmful concentrations and raise the osmotic pressure of the soil solution, which strongly inhibits the development of some crops (flax, maize), especially at the beginning of growth. In sufficiently humid regions, particularly on light soils, the nitrogen applied in the form of nitrates may be leached out and contaminate rivers and lakes. In irrigated regions of Central Asia, ammonia and ammonium-nitrate fertilizers are rapidly nitrified, and the nitrate nitrogen is leached downward (during watering) from the root zone or upward (after watering) to the surface. As a result of the rapid nitrification of the ammonium nitrogen in fertilizers with its subsequent denitrification, sizable amounts of nitrogen in the gaseous form are lost.

All this reduces the uptake of nitrogen by plants from fertilizers and lowers their effectiveness. Consequently, research workers have been trying in recent years to develop sparingly soluble fertilizers whose nitrogen is slowly solubilized and gradually taken up by plants throughout the vegetation period.

Slow-acting fertilizers are synthesized by condensing urea with aldehydes such as formaldehyde, acetaldehyde, crotonaldehyde, isobutyraldehyde, and others. The products include urea-formaldehyde fertilizer, or urea-form (UF) containing 38-40% nitrogen (including 28-32% water-insoluble nitrogen), crotonylidenediurea (CDU) containing about 32% nitrogen, isobutylidenediurea (IBDU) containing 31% sparingly soluble nitrogen, urea-formacetaldehyde (UFAA), and others.

The difficultly soluble forms of fertilizers are promising for high-rainfall regions and irrigated lands, especially for cultivation of cotton, tea, citruses, and grazing crops, as well as the grass of sports grounds and lawns where nitrogen is applied at high rates several times.

When applied at usual rates, these fertilizers are less effective within the first year than urea. However, at lib-

eral rates, they do not increase the soil solution concentration, their nitrogen is almost unleachable and its losses due to denitrification are minimal, yet it is taken up by plants over a longer period of time as these fertilizers gradually break down. In this case, apart from adequate nitrogen nutrition of the first crop, considerable aftereffect on subsequent crops is observed.

As regards other crops, for example vegetables and cereals in the Non-Black Earth zone, these fertilizers can be applied at high rates once a year or every two to three years without any danger of nitrogen leaching.

A disadvantage of slow-acting fertilizers is their prohibitive cost as compared to conventional readily soluble nitrogen fertilizers, the difference in cost being hardly compensated by the savings from single application. Besides, the rate at which nitrogen is liberated from the fertilizer does not always correspond to that at which it is taken up by most crops throughout the vegetation period, hence the lower effectiveness of such fertilizers, as compared to urea, in the year of application.

In some countries, attempts are being made to slow down the dissolution of nitrogen fertilizers by coating their granules with thin films of organic (polymeric) or inorganic (elemental sulphur) materials. The granules of these fertilizers gradually release nitrogen which is taken up by plants as the sulphur coating gets oxidized and dissolves.

Experiments indicate that application of sulphur-coated urea holds promise for rice, permanent meadows and pastures, vegetables and cucurbitaceous crops, especially in high-rainfall and irrigated regions. In the case of grain crops, sulphur-coated urea loses its advantages over soluble fertilizers. Because of the high cost of sulphur-coated urea and high sulphur requirements for its production, this fertilizer is used on an extremely limited scale.

5.10 Uptake of Fertilizer Nitrogen by Plants and Its Transformations in the Soil

Agrochemical studies by the tracer (isotope) method have shown that after application of nitrogen fertilizers plants grown in experimental fields take up almost 30 to 40 per

cent more nitrogen than on control plots, the amount of nitrogen taken up directly from the fertilizer being much less than was previously believed (Table 5.6).

Table 5.6. Uptake of Soil-Derived and Fertilizer Nitrogen by Plants (experimental results of the agrochemical department of the Timiryazev Agricultural Academy in Moscow)

Fertilizer	Taken up from				Fertilizer nitrogen balance (% of applied amount)	
	soil		fertilizer (% of applied amount)			
	% of total removal	% of control	difference method	isotope method	fixed in the soil	lost
Greenhouse experiments (averaged over 12 experiments)						
$(NH_4)_2SO_4$	49	143	74	60	19	20
$NaNO_3$	47	133	75	61	12	27
Average	48	138	74	60	—	—
Field experiments (averaged over 11 experiments)						
$(NH_4)_2SO_4$	67	134	60	39	44	17
$Ca(NO_3)_2$	65	139	67	42	25	32
Average	66	136	64	41	—	—

The experiments conducted at the agrochemical department of the Timiryazev Agricultural Academy in Moscow and other research institutions indicate that, when grown in the field, plants take up directly from the fertilizer only an average of 40% (varying from 30 to 50%) nitrogen of the applied amount, the nitrogen utilization factors with different forms of nitrogen fertilizers being essentially the same, and the only differences occur when the application conditions were extreme. The difference between the fertilizer nitrogen utilization factors determined by the difference method (60-70%) and its actual uptake determined by the isotope method (30-50%) ranges from 20 to 30 per cent, on the average, of the applied amount. This difference takes into account the additional uptake of soil-derived nitrogen after application of nitrogen fertilizers, caused by intensified mobilization of the nitrogen from the organic matter of the

soil. The additional soil-derived nitrogen uptake compensates for the incomplete uptake of nitrogen directly from the applied fertilizers. This is why the nitrogen utilization factors determined by the difference method are usually higher than those determined with the aid of ^{15}N for they include not only the uptake of nitrogen directly from the fertilizer (averaging about 40%), but also the additional uptake of nitrogen from the soil.

Hence, for practical purposes (calculation of the nitrogen balance, nitrogen fertilizer rates, etc.), one must use the utilization factors determined by the difference method since they represent the overall uptake of nitrogen by plants after application of nitrogen fertilizers.

The ratio between the soil-derived and fertilizer nitrogen in crops and its role in plant nutrition may vary widely depending on such factors as fertilizer rates, soil properties, cultural state of the soil, liming, and irrigation. For example, in field experiments (Table 5.6), soil-derived nitrogen accounted for an average of 66 per cent of the total removed amount, varying from 20 to 70 per cent in different experiments, while fertilizer nitrogen accounted for 34 per cent, varying from 30 to 80 per cent. Of all the nitrogen removed by crops, that of fertilizer increases and that of the soil decreases on humus-proof undercultivated soddy podsolic soils and in the case of high rates of nitrogen fertilizers.[1]

Experiments with ^{15}N have also shown that a sizable amount of fertilizer nitrogen (50-60% in field experiments) is not taken up by plants in the year of application, some nitrogen being lost from the soil and the rest being fixed in an organic form. Biological fixing of nitrogen is more pronounced in the case of ammonia fertilizers and urea (about 40% of the applied amount) as opposed to nitrates (20%). It becomes especially pronounced when large quantities of nitrogen-poor but cellulose-rich organic substances (crop residues, straw of cereals, straw manure, etc.) are ploughed down. The fertilizer nitrogen fixed in an organic form is mineralized slowly and taken up in insignificant amounts by the subsequent crops (which is precisely what accounts for the weak aftereffect of nitrogen fertilizers): two to three per cent of the applied nitrogen and five to ten per cent of the nitrogen fixed within the first year, one to two and three to six

per cent, respectively, within the second year, and even less within the following years, ultimately reaching the humus nitrogen uptake rate.

As a result of slow mineralization of the immobilized nitrogen and its partial uptake by subsequent crops, the fertilizer nitrogen utilization factors added up over six to seven years increase by eight to ten per cent, as compared to the tabulated utilization factors determined in the year of application.

Most of the incorporated fertilizer nitrogen is lost from the soil in gaseous form (N_2 and N_2O) after denitrification. The gaseous nitrogen losses are more pronounced from nitrates as opposed to ammonia fertilizers and urea. In the year of application, these losses from a soil with vegetative cover average 20 per cent with ammonia fertilizers and 30 per cent with nitrates. Losses from fallow soils become disproportionately high, reaching 50, 60 and more per cent.

The volatilization of fertilizer nitrogen from the soil, associated with its nitrification followed by denitrification, is the main reason why the utilization factors and effectiveness of nitrogen fertilizers decrease, if it is remembered that the leaching of fertilizer nitrogen in nitrate form throughout the vegetation period is usually minimal (less than 1% of the applied amount).

To minimize nitrogen losses and enhance the effectiveness of nitrogen fertilizers, it is extremely important to apply them at the right time, at optimal rates and ratios to other fertilizers in combination with a rational tillage system, crop rotation, and proper irrigation.

One of the ways to reduce soil-derived and fertilizer nitrogen losses due to denitrification and leaching of nitrates as well as to prevent contamination of rivers and lakes with nitrates and to minimize their content in the farm produce is through employment of nitrification inhibitors. These chemicals (organic compounds of the chloropyridine, pyrimidine, and other types) applied to the soil at rates ranging from 0.5 to 2 kg per hectare together with ammonia fertilizers inhibit nitrification of ammonium fertilizers and urea for as long as 1.5 to 2 months and keep the inorganic nitrogen of the soil and fertilizers in ammonia form. By doing so, the inhibitors cut down nitrogen losses due to volatilization and

leaching of nitrates by a factor of 1.5 to 2. Application of nitrification inhibitors is particularly effective in irrigated regions with cultivation of cotton and rice, as well as in high-rainfall or irrigated regions with cultivation of other crops.

5.11 Effectiveness of Nitrogen Fertilizers in Different Soil and Climatic Zones

Nitrogen fertilizers are a decisive factor of high crop yields on most soils of the USSR. It has been established that each ton of fertilizer nitrogen accounts for additional 10 to 15 tons of grain, 20 to 30 tons of meadow grass hay, 30 to 40 tons of sugar beet, about 2 tons of flax fibre, and 5 to 6 tons of cotton. Nitrogen fertilizers not only increase yields, but also improve the crop quality by raising the protein content in grain and fodder. They are especially effective in humid parts of the Non-Black Earth zone, on nitrogen-deficient soddy podsolic soils. Their effectiveness is also high on grey forest-steppe soils and leached chernozems of the western regions (Table 5.7).

Table 5.7. Potato Yield Increases Due to Different Fertilizers (experimental data from the USSR Research Institute of Fertilizers and Agronomical Soil Science)

Soils	Number of experiments	Yiel without fertilizer (cent/ha)	Increase due to fertilizer (cent/ha)			
			NPK	N	P	K
Podsolic sandy loam	23	117	60	35	13	16
Podsolic loam	8	154	69	39	18	28
Grey forest	6	159	73	43	10	9
Leached chernozems	10	203	56	31	20	13

Application of phosphorus and potassium fertilizers to soddy podsolic and grey forest soils without nitrogen ones usually produces no tangible effect. As far as these soils are concerned, nitrogen fertilizers account for about 60 per cent of

the overall yield increase due to fertilizers. As one goes from north southwards and from west eastwards, that is, towards low-rainfall regions, the effectiveness of nitrogen fertilizers decreases.

In the southern steppe regions with deep, ordinary, and southern chernozems containing a lot of nitrogen but little moisture and especially south-eastern regions with chestnut and light chestnut soils, yield increases due to nitrogen fertilizers are less spectacular than in the humid regions of the Non-Black Earth and Forest-Steppe zones. However, when appropriate measures are taken to accumulate and retain moisture in fields (snow retention, timely ploughing in autumn, etc.), moderate rates of nitrogen fertilizers are quite effective in these regions. The effectiveness of nitrogen fertilizers in the southern and south-eastern steppe regions is considerably enhanced by irrigation. Application of nitrogen fertilizers is a prerequisite for high yields of all crops on irrigated sierozems and other soils of Central Asia and Transcaucasia.

Nitrogen fertilizers also ensure high yield increases in the high-rainfall regions of North Caucasus and subtropical regions.

5.12 Application of Nitrogen Fertilizers to Various Crops

Nitrogen fertilizers are applied to all farm crops. Legumes present a special case: they make use of the atmospheric dinitrogen fixed by nodule bacteria. However, at the beginning of growth, when nodule bacteria are still underdeveloped, legumes need a source of available nitrogen in the soil. Therefore, legumes, too, especially pulses, responds well to application of nitrogen fertilizers at small rates (30 to 40 kg/ha). On cultivated soils, particularly after manuring to enhance the growth of the legumes' precursor, they thrive even without nitrogen fertilizers.

Grain crops are highly sensitive to nitrogen fertilizers which promote the development of vegetative and reproductive organs, increase the tillering energy, grain yields, and protein content in the grain. The yield of these crops is giv-

en a particular boost when nitrogen fertilizers are applied with irrigation and in sufficiently humid regions.

Most grain cereals take up nitrogen at the early stages of their growth. For example, winter wheat at the tillering stage takes up half, and at the heading stage two thirds, of the total nitrogen required. Winter rye takes up most of nitrogen at an early age. In contrast with winter wheat, the spring variety has a shorter nutrition period. Its uptake of nitrogen is most intensive between the tillering and milky ripeness stages. The nutrition period of barley is even shorter than that of spring wheat.

Maize, millet, buckwheat, oat, and rice are characterized by an extended nutrition period, taking up nitrogen and other nutrients also at late growth and development stages, i.e. before the gold ripeness stage in the case of maize and before the flowering and ripening stages in the case of millet.

In order to create favourable conditions for the growth of *winter crops* on occupied fallow, especially after late-harversted precursors, nitrogen fertilizers must be applied in autumn at rates ranging from 30 to 60 kg/ha before seeding (during ploughing or preseeding cultivation). When winter crops are sown after clover and on properly tilled clean fallow, application of nitrogen fertilizers prior to seeding is usually not required. To increase the yields of winter cereals, it is extremely important to dress them with nitrogen fertilizers in early spring, which is especially effective in the Non-Black Earth and Forest-Steppe zones. Supplemental application of nitrogen at a rate of 20 to 30 kg/ha in early spring increases the grain yield in these zones by an average of three to four centners and, in many cases when advanced farming practices are implemented, six to eight centners per hectare (Table 5.8).

Dressing with nitrogen is also effective on chernozems. For example, dressing of winter rye in spring with ammonium nitrate applied at a rate of 30 kg of the active ingredient per hectare to deep weakly alkaline chernozem increased the yield by 25 per cent (without dressing, the yield was 18.4 centners and, after dressing, 23.0 centners per hectare). According to the USSR Research Institute of Fertilizers and Agronomical Soil Science, increasing the rate of nitrogen used for dressing from 30 to 60 kg/ha ensures a much higher yield

increase (from 5.3 to 7.4 centners per hectare on the average over a two-year period), although the crop return from the second 30 kg is less than that from a single dose. The high effectiveness of dressing with nitrogen in early spring stems from the fact that after hibernation winter crops become too weak, their intensive growth and uptake of nitrogen beginning in early spring, while mobilization of the soil-derived

Table 5.8. Effectiveness of Dressing Winter Crops with Nitrogen (according to Naidin)

Soils	Yield on control plot (cent/ha)	Yield increase due to dressing (cent/ha)	Number of experiments
Soddy podsolic sands and sandy loam	16.1	3.3	6
Soddy podsolic loam	18.8	4.3	18
Grey forest loam	11.8	3.5	4
Leached chernozems of the Ukrainian SSR and western parts of the Central Non-Black Earth zone	20.1	2.6	3
Leached and deep chernozems of eastern regions of the European part of the RSFSR	28.4	1.0	6

nitrogen during this period is minimal because of the low temperature and high moisture content of the soil. Depending on the desired height of the crop stand, the nitrogen rate in early spring dressing may vary from 30 to 90 kg/ha.

Apart from dressing in early spring, nitrogen fertilizers are also used to dress winter wheat (20-30 kg of nitrogen per hectare) much later (after heading). In this case, wheat is sprayed with a urea or ammonium nitrate solution. The late foliar dressing usually does not increase yields but perceptibly improves the crop quality by raising the protein and gluten content in wheat kernels.

Spring grain crops (wheat, barley, oat, millet) are treated with nitrogen fertilizers at average rates of 30 to 60 kg/ha. They are placed in autumn during ploughing or (in humid regions) preseeding cultivation. The spring cereal to be

treated with nitrogen in the first place is wheat (if it does not follow clover or alfalfa).

As far as *maize* is concerned, nitrogen is applied at rates ranging from 60 to 90 kg/ha, depending on soil fertility and precursors, the moderate doses being applied before sowing, while in the case of high dosage (90 kg and above), most of the fertilizer is applied before sowing and the rest (20-25 kg) is used for dressing during the first inter-row tillage. When spring cereals, especially wheat, are grown on chernozems and chestnut soils, nitrogen is applied liberally at rates of 60 to 90 kg/ha.

The optimal nitrogen rate for *rice* is 120 to 150 kg/ha, half the rate being applied when the paddy is reploughed in spring before sowing or during cultivation, and the other half is used for dressing once or twice.

The best forms of nitrogen fertilizers in this case are ammonium sulphate and urea.

Cotton requires much more nitrogen than grain crops. Most of it is taken up by cotton plants during the second half of the vegetation period, from the end of budding to the boll opening stage. Hence, to meet the nitrogen requirements of cotton, one must resort to basal and supplemental applications.

Irrigation of cotton fields substantially alters the temperature and water regimes of the soil. Transitions from waterlogging of the soil during irrigation to drying during the irrigation interval strongly affect the biochemical and chemical soil processes. Specific conditions are created for the dynamics, composition, and concentration of the soil solution, as well as migration of the soluble salts, and plants take up the fertilizer nitrogen at different rates. In the cotton-growing regions of Central Asia, ammonium salts are nitrified intensively, and the nitrogen of all fertilizer forms is mobilized to the same extent. To immobilize nitrogen and localize it in the root layer of the soil, it has been recommended to apply organic and inorganic fertilizers together. The ammonification and nitrification processes are in this case extended over a longer period of time, which is extremely important for cotton, a crop with long vegetation and nutrition periods. Nitrogen fertilizers are placed under cotton during the vegetation period, part of them being incorporated before seed-

ing. If the application rates are relatively low, the entire amount of the fertilizer is applied to dress cotton during the vegetation period, preferably at the budding and flowering stages. At high rates, about a third of the fertilizer is applied before seeding, while the rest is used for dressing. In the case of first- and second-year cotton crops after alfalfa, nitrogen fertilizers are used only for dressing. The nitrogen rate is increased with each year so that eventually nitrogen fertilizers are partially used for basal application. The nitrogen rates for cotton depend on the desired yield, cultivation practices used, and soil and climatic conditions of the region. An average of 150 to 200 kg of nitrogen per hectare are usually applied. The preferable forms of nitrogen fertilizer for cotton are ammonium nitrate, ammonium sulphate, and urea.

Fibre flax is grown on soddy podsolic and grey forest soils. The critical period in the nitrogen nutrition of flax falls between the branching and budding stages. Nitrogen deficiency in this period leads to low yields and crop quality. Flax follows perennial leguminous grasses and other precursors in crop rotation.

When flax does not follow perennial grasses, the average nitrogen rates of 40 to 60 kg/ha are applied before seeding; at a rate of 70 to 90 kg, part of it (20 to 25 kg) may be used for dressing flax at the branching stage. Flax grown the year after the leguminous precursor is adequately supplied with nitrogen, which is why nitrogen fertilizers are applied before seeding in small quantities (20 to 30 kg of nitrogen). The main forms of nitrogen fertilizers for flax include ammonium nitrate and urea.

Hemp calls for heavy application of fertilizers, primarily nitrogen ones. The optimal rate for most soils is 90 to 120 kg of nitrogen per hectare, chernozems being treated at a rate of 60 to 90 kg/ha. As nitrogenous organic substances undergo mineralization in cultivated peaty soils, the nitrogen rate is reduced to 30 kg. The nitrogen rate is also lowered when fertilizers are combined with manure. All of the nitrogen fertilizers rated for hemp are applied in spring during the preseeding cultivation.

Sugar beet requires moderate amounts of nitrogen at the seed germination stage. Greater quantities of nitrogen, es-

pecially in the ammonia form, may weaken the sprouts with their underdeveloped leaves. Later, when the plants develop strong roots and tops, the nitrogen requirements grow immensely. Finally, at the sugar accumulation stage, this nutrient becomes less important. The fertilizer system for sugar beet must be based on the biological characteristics of this crop. The basal fertilizer is placed in autumn during deep ploughing, while the row fertilizer is applied at low rates (8 to 10 kg of nitrogen per hectare) together with phosphorus fertilizers during seeding.

Drilling should preferably be done with sodium nitrate. It is better than other nitrogen fertilizers not only because of the nitrogen form, but also due to the positive effect of sodium.

At a rate of 120 to 150 kg of nitrogen per hectare, a small amount (20-25 kg) may be used for dressing at the early stages of sugar beet development. Delayed dressing may cause accumulation of nitrous compounds in roots, particularly non-protein nitrogen, a decrease in sucrose content, and over-extended vegetation. Dressing of sugar beet with watering is extremely effective in terms of yield.

To harvest 300 centners of sugar beet from a hectare of non-irrigated land and 500 centners from a hectare of irrigated land, the following nitrogen rates are used (in kg/ha): 60 to 90 in the case of basal application to chernozems, 90 to 120 for soddy podsolic soils, 120 to 150 in irrigated sierozems and chestnut soils, and 20 to 30 in the case of dressing.

Potato plants intensively take up nutrients after they start flowering. At the flowering stage, they have a well developed haulm, and tubers start to grow fast. Application of nitrogen fertilizers raises potato yields considerably. Higher yields are attained on soddy podsolic soils, while on grey forest soils and chernozems nitrogen fertilizers are not as effective.

Excessive nitrogen supply after flowering prolongs the vegetation period, intensifies the growth of haulm, causes tubers to develop second- and third-order stolons, and lower the crop quality.

Nitrogen fertilizer forms suitable for potatoes include ammonium nitrate and ammonium sulphate applied at a rate of 60 to 90 kg of nitrogen per hectare before planting. Some

of the fertilizer (15-20 kg N) is also applied locally during hole planting.

Tobacco is extremely responsive to nitrogen. To obtain a high yield of quality crop requires adequate supply of this plant with nitrogen. Apart from the nicotine content, the quality of tobacco is also dependent on the contents of proteins and carbohydrates, fats, resins, essential oils, as well as malic, citric, and other organic acids in leaves. Excess of proteinaceous substances and a heavy predominance of carbohydrates over proteins adversely affect the quality of tobacco.

The nitrate form of nitrogen enhances accumulation of citric and malic acids, whereas ammonia nitrogen promotes formation of more reduced products, such as essential oils.

A high level of nitrogen nutrition leads to an increased content of nicotine and proteins and also prolongs the vegetation period. The average rate of nitrogen for tobacco is 60 to 90 kg/ha. Most of it (60-70%) is applied in spring before planting, the rest being placed locally during planting.

Rustic tobacco is also highly sensitive to nitrogen application. Since it is necessary to maintain a high nicotine content in rustic tobacco, it is treated with nitrogen fertilizers at increased rates. Organic fertilizers are effective with respect to this crop as well. When combined with inorganic fertilizers, they provide for higher yields of rustic tobacco.

Nitrogen is an important factor of high yields of *tea* leaves. Treatment of tea plantations with nitrogen fertilizers increases the yield by 40, 50 and more per cent.

The best system for tea is a combination of organic and inorganic fertilizers. Recommended among inorganic fertilizers are ammonium nitrate, ammonium sulphate, and ammonium-sodium sulphate at a rate of 150 to 200 kg of nitrogen per hectare. The fertilizer rate depends on soil properties, its humus content, and the shrub age. Fertilizers are applied twice: 60 per cent in early spring and 40 per cent in summer, between rows to a depth of 6 to 8 cm. On young plantations, nitrogen is applied in spring, using band placement at a distance of 8 to 10 cm from the root neck of the shrub, in amounts ranging from 40 to 60 kg per hectare.

Vegetable crops require a lot of nitrogen throughout the vegetation period.

The highest cabbage yield increase occurs in July and August (84% of the overall yield), when cabbage takes up high amounts of nitrogen.

The peak of nitrogen uptake by carrots is in late August and in September.

The rate of nitrogen uptake by cucumbers increases gradually, reaching the maximum at the ovary development stage. Then, the uptake of nitrogen slows down dramatically.

Nitrogen fertilizers are also important for increasing the yield of tomatoes.

Vegetables grown in the Non-Black Earth zone are treated with nitrogen fertilizers at rates ranging from 60 to 120 kg of nitrogen per hectare, provided 20 to 30 tons of manure are applied at the same time.

Fruit and berry crops are the most sensitive to nitrogen fertilizers. The latter are highly effective when applied separately as well as in combination with phosphorus-potassium fertilizers. Treatment with nitrogen enhances the growth of vegetative organs, formation of fruit buds and ovaries, the size of fruits and their quality.

Fertilizers must be incorporated deep into the soil, as closely as possible to the bulk of fibrous roots. This is achieved by placing fertilizers in holes and ditches or their injection to a depth of 50 cm and more. At the fruit-bearing stage (apple, pear, cherry, etc.), the usual rate of annually applied nitrogen is 60 to 90 kg, and in the case of southern crops (plumb, peach, hazel nut, olive, persimmon, etc.), it is 60 to 90 and sometimes even 120 kg per hectare. Depending on soil fertility, berry crops (strawberry, currant, gooseberry etc.) receive 45 to 60 kg of nitrogen per hectare.

Overnutrition of fruit and berry crops with nitrogen is not desirable because it stimulates vegetative growth at the expense of fruit bearing.

Forage cereal grasses are also extremely responsive to nitrogen fertilizers. The productivity of hay fields and cultivated pastures fertilized with nitrogen increases appreciably along with hay yield and quality. Nitrogen fertilizers are applied to irrigated lands at rates of 120 to 240 kg per hectare, three to five times before watering.

Chapter 6

Phosphorus Fertilizers

6.1 Phosphorus in the Life of Plants

Oxidized phosphorus compounds are an absolute necessity for all living organisms. Not a single living cell can survive without phosphoric acid. Nucleoproteins constituting the essential substance of cell nuclei contain phosphoric acid. Nucleoproteins are protein compounds with nucleic acids, including phoshoric acid. Just as all proteinaceous substances, nucleic acids are high-polymer colloidal compounds. Distinction is made between ribonucleic (RNA) and deoxyribonucleic (DNA) acids. Their structure is highly complex although they consist of only four basic components—nucleotides. The structure of nucleic acids bears an "imprint" of the hereditary traits of an organism, which governs the synthesis and structure of protein molecules in the progeny. Proteins, in turn, and enzymes in particular influence the synthesis of RNA and DNA.

The phosphorus content (in terms of P_2O_5) in nucleic acids is in the neighbourhood of 20 per cent. Nucleic acids are present in every plant cell, in all tissues and organs. Their content in leaves and stalks reaches 0.1-1 per cent of dry matter, being higher in young leaves and growing points as opposed to old leaves and stalks. The greatest amounts of nucleic acids are found in seed germs, pollen, and root tips.

Phosphorus is also present in some other organic compounds of plants, such as phytin, lecithin, sugar phosphates, and others. Phytin (calcium-magnesium-potassium salt of inositol hexa-phosphoric acid) is an ester-like compound of the hexatomic alcohol inositol and hexa-phosphoric acid, containing 27.5% P_2O_5. Phytin ranks first among other phosphorus compounds in terms of their content in the seeds and vegetative organs of some farm crops.

Seeds contain more phytin than young plant organs and tissues. Its content is 1 to 2% dw in the seeds of leguminous and oil-producing crops and 0.5 to 1% dw in those of cere-

als. Phytin is present in seeds as a reserve substance, and the constituent phosphoric acid is utilized during their germination.

Lecithin is essentially a phosphatide, one of the waxy substances found in the cytoplasm of all active plant cells, accumulated primarily in seeds. It contains 1.37% P_2O_5 and is a derivative of diglyceride phosphoric acid whose magnesium and calcium salts are present in leaves.

Phosphatides play a major biological role, being localized in the phospholipid membranes which regulate the permeability of cell organelles and the plasmalemma to various substances.

Sugar phosphates are phosphorus compounds always present in all plant tissues. The role of these compounds is particularly important in respiration, synthesis of complex carbohydrates (sucrose, starch, etc.) from simpler ones, photosynthesis, mutual transformations of carbohydrates, and other processes.

Sugar phosphates are highly labile and more reactive, as compared to free sugars, owing to association with phosphoric acid. The content of sugar phosphates varies markedly depending on the age of plants, conditions of their nutrition, and other factors, from 0.1 to 1.0% dw.

Thus, phosphorus is a constituent of many organic compounds of biological importance, without which plants cannot live. This, however, is but one aspect of the role played by phosphorus. Synthetic processes, such as biosynthesis of proteins, fats, starch, and sucrose, require large amounts of energy provided by so-called high-energy compounds. The latter feature high-energy bonds, and the free energy of their hydrolysis is 25 to 67 kJ/mole, which is much higher than the free energy of hydrolysis of ordinary ester bonds (8-12 kJ/mole).

At present, a great number of high-energy compounds are known, most of them containing phosphorus and having high-energy bonds whose formation involves phosphoric acid.

In spite of the large number of high-energy compounds in living organisms, the predominant role is played by adenosine triphosphoric acid (ATP). It is the main recipient of the energy liberated during breakdown of organic compounds

in cells, and the chief carrier of this energy required for synthetic processes.

ATP consists of a residue of the nitrous base adenine combined with that of the carbohydrate ribose and three residues of phosphoric acid. It has two high-energy phosphate bonds. As an energy carrier, ATP is involved in the biosynthesis of proteins, fats, starch, sucrose, asparagine and glutamine, some amino acids, and many other compounds.

In young, rapidly growing plants, phosphorus is localized mainly in the meristematic tissue. It moves easily in plants being translocated from older into younger tissues or, in other words, reutilized. As crops mature, most of the phosphorus assimilated by plants is concentrated in seeds and fruits (up to 50% in the kernels of cereal crops).

Inorganic phosphates are not accumulated in sizable amounts in vegetative organs, to say nothing of seeds, if the phosphorus nutrition of the plant is normal. However, excess of easily available phosphorus in the soil or delayed application of phosphorus fertilizers, as well as deficiency of nitrogen and other nutrients, may lead to accumulation in plant tissues of the inorganic phosphates unused in the synthesis of organic phosphorus compounds.

In plants, organic phosphorus compounds are heavily predominant, including phytin (Table 6.1).

Table 6.1. Forms of Phosphates in Plants (in % P_2O_5 dw)

Crop	Total phosphorus	Organic phosphorus					Inorganic phosphorus	% of total phosphorus	
		lecithin	phytin	nucleoproteins	others	total		organic	inorganic
Wheat (grain)	0.860	0.032	0.609	0.130	—	0.771	0.089	89.6	10.4
Clover (hay)	0.554	0.050	0.300	0.050	0.084	0.484	0.070	87.0	13.0

Of particular interest is the distribution of phosphorus among cell structures. As was demonstrated on clover leaves, the phosphorus content was (in % of its total amount):

50 in the cytoplasm, 21 in the nucleus, 19 in plastids, and 10 in mitochondria.

Quite a lot of phosphorus (15.1% in winter rye and 22% in lettuce, in terms of total content in the leaf) is present in chloroplasts which serve as sites of photosynthesis.

6.2 Sources of Phosphorus for Plants

The chief source of phosphorus for plants under natural conditions is orthophosphates. However, it has been established that pyro- and polyphosphates in general may also be used by all crops after hydrolysis. Metaphosphates can be assimilated even without hydrolysis, yet most of them are hydrolyzed since they are usually represented by polymers such as $(KPO_3)_n$.

Being tribasic, orthophosphoric acid may give off three anions: $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. In the case of a weakly acidic reaction (pH) of the medium, prevailing in the cultivation of most crops, the first anion occurs most widely of the three, although the second one may also be encountered, while the third has virtually nothing to do with plant nutrition (Table 6.2).

Table 6.2. Ratio (%) Between Non-Dissociated H_3PO_4 Molecules and Their Anions at Different pH Values

Acid, ions	pH			
	5	6	7	8
H_3PO_4	0.10	0.01	—	—
$H_2PO_4^-$	97.99	83.68	33.90	4.88
HPO_4^{2-}	1.91	16.32	66.10	95.12
PO_4^{3-}	—	—	—	0.01

When the pH value of the soil solution varies from 5 (soddy podsolic soils) to 7 (chernozems), plants are supplied primarily with $H_2PO_4^-$ and, to a lesser extent, with HPO_4^{2-}. The soil contains only orthophosphates, although the currently used compound fertilizers may also contain meta-, pyro-,

and polyphosphates. Their availability to plants will be discussed in what follows (see "Compound Fertilizers").

However, a group of crops is known which is characterized by an ability to take up phosphorus also when the soil contains only tricalcium phosphates or even more complex and less soluble natural phosphorites. These crops include lupine, buckwheat, mustard, and also pea, sweetclover, sainfoin, and hemp, the latter four taking up phosphorus from phosphorites to a lesser degree than the former three.

The ability of these crops to be sustained by difficultly soluble phosphates stems primarily from the acidity of the root exudates. It has long been demonstrated that the pH value of the solution film enveloping the root hairs of lupine is 4 to 5, while that of a similar film around clover roots is 7 to 8. These values explain why lupine dissolves phosphorite and clover does not. However, the reaction of the cell sap in roots does not correlate with the capacity of plants to dissolve phosphorite because in most crops the pH value of the cell sap varies from 5 to 7, that is, approaches the neutral point. Cell sap with a strongly acidic reaction is found only in dock, begonia, and rhubarb. Their cell sap has pH 1.2-1.5.

Chirikov noted the weight ratio between CaO and P_2O_5 at the flowering stage of plants capable of being nourished by poorly soluble phosphates and those lacking this capacity. It was found that in the case of lupine, buckwheat, and mustard this ratio exceeds 1.3, while in the case of cereals it is below 1.3. Thus, the more intensive displacement of calcium from the external solution in the case of plants belonging to the first group speeds up the transfer of phosphorite-derived phosphoric acid into the solution, which allows ground phosphorite to meet the phosphate-ion requirements of the crop more fully. Taking up little calcium, crops of the second group thereby slow down the dissolution of phosphorite so that these crops, and they are in the majority, fail to satisfy their demand in phosphoric acid from phosphorites and, in general, poorly soluble phosphates.

Of course, there are exceptions to this rule. For instance, in fibre flax $CaO : P_2O_5 = 1.8$, this ratio increasing further as plants senesce, yet this crop cannot take up phosphorus

from phosphorite. The same applies to Italian millet. Hence, the $CaO : P_2O_5$ ratio in the ash of plants cannot be considered as the only precondition for nutrition of a crop from poorly soluble phosphorus sources.

Of equal importance are such external factors as concomitant fertilizers (to be more precise, their physiological acidity) and potential acidity of the soil.

Even less available to plants are neutral and especially basic salts of trivalent cations and orthophosphates, accounting for most phosphates in acid soils ($AlPO_4$, $Al_2(OH)_3PO_4$, $FePO_4$, $Fe_2(OH)_3PO_4$, etc.).

Can higher plants assimilate organic phosphates? Experiments aimed at elucidating the assimilation of phosphorus from organic compounds give no reason to regard the latter as directly available to plants in sizable amounts without preliminary breakdown of mineral phosphates by the enzymes of microorganisms or root systems.

Phosphorus deficiency in plants manifests itself in the bluish green coloration of leaves, often with purplish or bronze hues (indication of retarded protein synthesis and sugar accumulation). Leaves often diminish in size and become narrower with their edges curling upwards (potato). They are darker than leaves normally supplied with phosphorus. The leaves of phosphorus-deprived tobacco form a right angle with the stem, their blades becoming longer and narrower.

Phosphorus deficiency stunts crop growth and delays maturation.

It should be pointed out, however, that excess phosphorus is not good for plants either for they cannot properly assimilate it because most phosphates are in inorganic form, especially in vegetative organs (organic compounds account for 90% phosphate in seeds). When phosphorus is excessive, crops mature early and their yields are low.

Phosphorus in plants is heavily predominant in seeds and, generally speaking, in the commercially valuable part of crops, as opposed to straw and other useless parts, such as vegetative organs. Potatoes are an exception.

The content of phosphorus in plants, soil, and fertilizers is usually expressed in terms of its pentoxide, P_2O_5 (Table 6.3).

Table 6.3. Phosphorus Content in the Main Organs of Some Crops

Crop	P_2O_5 content (%)		Remarks
	in grain, tubers	in straw, haulm	
Winter wheat	0.85-1	0.2	At harvesting (14.3% moistrure in grain, 16% in straw)
Pea	0.9-1.1	0.35	Ditto
Potato	0.14	0.16	Fresh before harvesting (75% moisture in tubers, 77% in haulm)

The absolute removal of phosphorus by the valuable part of the crop is always higher, as compared to the useless parts (which will be shown in what follows).

The effect of phosphorus on the vital activity of plants is manifold. Adequate phosphorus nutrition not only raises crop yields considerably, but also perceptibly improves crop quality. The percentage of grain in cereals increases, and it becomes richer in starch and sometimes proteins. Fruits and taproots accumulate more carbohydrates. Fibre crops develop longer, stronger and finer fibre.

Unlike nitrogen, phosphorus accelerates the development of crops, which minimizes the danger of their being affected by dry winds in southern regions and by frosts in northern ones (in the case of spring cereals in early autumn). The increased content of soluble carbohydrates in the cell sap lowers the freezing point of plants, which improves the winter hardiness of winter crops and perennial leguminous grasses after application of phosphorus fertilizers in autumn. Also improved are the strength of straw and the lodging resistance of cereals.

6.3 Chemical Fixation of Phosphates by Soils

The capacity of soils to absorb phosphoric acid is so high that it takes five to ten tons of P_2O_5 per hectare to completely saturate the soil. Remember that the overall P_2O_5 reserves in the arable layer amount to only three to six tons per

hectare. Hence, saturation of the soil with phosphates is not feasible not only from the economic standpoint, but also in purely technical terms. Yet, about 40 years ago, when it was feared beyond reason that red soils permanently fix the applied phosphorus fertilizers, that is, convert them into absolutely unavailable compounds, serious suggestions were made to place three tons of these fertilizers per hectare at once so as to ensure the effectiveness of subsequent normal rates of superphosphate at tea plantations.

But even then agrochemists proposed another solution: application of ground phosphorite to acid soils instead of superphosphate and making use of the soil acidity to break down the phosphorite. In the case of superphosphate, emphasis was placed on the importance of its local application which rules out interaction between the fertilizer and most of the soil, thereby minimizing the chemical fixation of phosphoric acid.

Years of experience have proved agrochemists right: application of phosphorites to the highly acidic soils of tea plantations has turned out to be equivalent to that of superphosphate. As regards superphosphate, it is placed between rows, if necessary, without being mixed with large quantities of soil. The previously applied phosphorus fertilizers have also been found to have an unusually persistent aftereffect on both red and subtropical podsolic soils, which attests to the groundlessness of the fear that phosphates may be permanently fixed even in such soils rich in sesquioxides.

These fears have been especially exaggerated in regard to other soils, particularly those whose pH falls between weakly acidic and weakly alkaline. As water-soluble phosphates are incorporated into such soils with fertilizers, they eventually turn to dicalcium and dimagnesium phosphates ($CaHPO_4 \cdot 2H_2O$, $MgHPO_4$), as a result of chemical fixation, and long remain in this form available to all crops. Later, the hydrogen ion remaining in the disubstituted salt is replaced by calcium or magnesium to yield trisubstituted phosphates of these metals, $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$, as well as more basic phosphates. But even these salts, while being in the freshly formed amorphous state, retain their property of being perceptibly dissolved in weak acids, hence, remain partially available to plants. Only in the course of

time, as they "age", do trisubstituted and more basic phosphates become unavailable to most crops.

The situation is aggravated in acid soils where, as has already been mentioned above, iron and aluminium phosphates emerge at the expense of water-soluble calcium phosphates. However, this dangerous tendency may be controlled by liming such soils, whereby phosphates of sesquioxides are converted back into calcium and magnesium phosphates, this effect of lime persisting over a period of time sometimes longer than a decade.

Analyses of leached chernozems at the Mironovka (Kiev Region) and Sumy experimental stations, carried out after many years of superphosphate application, have shown that about half the phosphates applied earlier were in the form of salts extractable by CO_2-saturated distilled water; there is no doubt that these are phosphorus forms readily available to all crops.

In many cases, the weak aftereffect of phosphorus fertilizers may be explained not by permanent fixation of phosphoric acid ions by soils, but by nitrogen and potassium deficiency. Application of these nutrients immediately enhances the aftereffect of phosphates.

It is also known that systematic application of phosphorus fertilizers over a long period of time at heavy rates (i.e. several times exceeding the rates of phosphorus uptake by crops) may lead to accumulation of such large amounts of available phosphates in the soil that the newly applied phosphorus fertilizers cease to be effective.

It goes without saying that such plots and fields need not be treated with phosphates as long as crops may be sustained by the aftereffect of the easily available phosphorus reserves accumulated in the soil as a result of many years of its incorporation with fertilizers.

Elucidation of the mechanism of soil phosphatization suggests two conclusions: firstly, we have another proof that phosphates are not permanently fixed in the soil in sizable amounts; secondly, it provides a vivid illustration of the usefulness of agrochemical soil analyses in optimization of fertilizer application schedules. Without such analyses it would be impossible to identify field plots with different contents of available phosphorus, hence, to establish cor-

rect phosphorus rates. Prolonged application of phosphorus fertilizers in Rothamstead has made their aftereffect last as long as 50 years.

Phosphates in the soil are affected by organic matter, moisture content, and temperature (in addition to the above-mentioned effects of the argillaceous mineral species, sesquioxide, and soil reaction). It has been established that sodium humates render calcium phosphates in the soil more mobile, yet their influence does not extend to sesquioxide phosphates. It has also been found that addition of humus (extracted from peat) intensified the effect of calcium monophosphate on red soil in a greenhouse experiment with oat. What we must be dealing with in this case is adsorption of organic anions by positively charged colloidal soil particles (including those of sesquioxides), which does not allow them to fix the phosphate anion and thus makes it more readily available to plants. This is due to the fact that many organic acids (pyruvic, citric, maleic, malonic, lactic, oxalic) fix aluminium and iron cations in the acidic medium so that they cannot make phosphate ions poorly soluble and unavailable.

The practical conclusions drawn from these findings are also known. They boil down to application of a mixture of humus with superphosphate (or complete fertilizer), which often substantially improves the effectiveness of phosphorus and other nutrients. It should be pointed out that the effect of humus is manifold: it minimizes chemical fixation of phosphate ions by soil particles (especially sesquioxides), and, as an adsorbent, it increases the buffering capacity of the soil in those parts where it contains humus, thereby mitigating the harm inflicted by the physiological acidity of ammonia and potassium salts; finally humus itself is a source of nutrients for plants (nitrogen, phosphorus, sulphur, etc.) if its application rate is sufficient.

While studying the dynamics of soil phosphates under conditions of varying moisture content, Lebedyantsev found that drying of chernozem leads to a drastic mobilization of phosphates, which is beneficial for soil fertility. In explaining this phenomenon, Frantseson demonstrated that rapid moistening of a dried soil initiates vigorous breakdown of soil aggregates. It is quite possible that exposure of new

internal surfaces drives the previously latent phosphorus compounds into solution. One of the results of such "unpacking" of soil aggregates is increased mobility of the organic matter of the soil.

Under actual farming conditions, soils become parched because of factors beyond the farmer's control, such as periods of drought. It has been noticed that after a dry year yields are often higher. It is hard to tell at present whether this is a consequence of improved phosphate regime of the soil. Desiccation of the soil sometimes enhances the mobility of its phosphates and their absorption. For example, before deep chernozem of the Voronezh Region was brought to an air-dry state, it absorbed four to five times more phosphoric acid from a weak calcium monophosphate solution than when moist. This may stem from the fact that all soils absorb more phosphates from solutions of a higher concentration. If this is so, in the case of liquid phosphorus fertilizers one should expect a more complete absorption of phosphoric acid by soils. The texture is also an important factor: particles larger than 0.01 mm in size virtually do not adsorb phosphates.

There are several reasons why phosphorus is less readily available than nitrogen and potassium even when its sources are soluble fertilizers and mobile soil reserves (from 10 to 15%). The governing factors are as follows: extremely weak diffusion of phosphate ions in the soil (as a result of their rapid chemical, physicochemical and biological fixation by soil components); insufficient expansion of the absorbing root system throughout the soil (according to some reports, only 1/250 of the soil volume is in contact with roots); predominantly low moisture content in the soil, which hinders further the already weak diffusion of phosphates in it.

Phosphates form less soluble forms with argillaceous soil varieties as opposed to light loams. Hence, the dissimilar effect of equal P_2O_5 rates on different soils, although in the case of an optimal moisture content the diffusion of phosphates in clayey soils may be more pronounced than in sandy ones.

Experiments have provided ample proof that phosphorus nutrition conditions are more favourable for plants (espe-

cially on acid soils) when phosphorus fertilizers are placed in a localized manner. This is normally achieved by band application of pelletized fertilizers.

It has been found that the interaction of superphosphate with the soil yields up to thirty phosphoric acid compounds differing widely in stability, solubility, and availability.

6.4 Phosphoric Acid Anions Undergoing Exchange Adsorption in the Soil

The argillaceous minerals present in the soil adsorb phosphate anions most intensively in an acidic medium. For example, illite (a mineral belonging to the hydromica group) was found to adsorb 9 meq of these anions per 100 g at pH 4.5, while kaolinite adsorbed 7.7 meq at pH 4. At pH 4, bentonite adsorbed 9.7 meq $H_2PO_4^-$. As is known, in terms of exchange adsorption of cations, the montmorillonite group of argillaceous minerals, including bentonite, is much superior to the kaolinite one. This, however, is not evident from the exchange adsorption of the phosphoric acid anion. This anomaly is explained by the fact that the gibbsite layer of montmorillonite minerals is confined on both sides by silicon-oxygen tetrahedra, while in kaolinite minerals tetrahedra confine this layer only on one side. $H_2PO_4^-$ ions can be adsorbed by argillaceous minerals in exchange for the OH^- groups of the gibbsite layer. There is a possibility, though, that these anions are adsorbed primarily as potential-determining ions.

Another possibility that has been suggested is formation of $[PO_2(OH)_2]^-$ tetrahedra that are retained on the surface of the argillaceous mineral crystal or even exchanged for silicon-oxygen SiO_4 tetrahedra. It has been speculated that chemical fixation of phosphate ions by hydrates of sesquioxides is accompanied by an exchange of the hydroxyl groups of these sesquioxides in a colloidal state for $H_2PO_4^-$; schematically, the reaction can be represented as follows:

$$\text{colloid of Al/Fe oxides} \begin{vmatrix} OH^- \\ OH^- \\ OH^- \end{vmatrix} + H_2PO_4^- \rightarrow \text{colloid of Al/Fe oxides} \begin{vmatrix} OH^- \\ OH^- \\ H_2PO_4^- \end{vmatrix} + OH^-$$

It has also been suggested that, apart from being adsorbed by positively charged colloidal soil particles, phosphoric acid anions may act as acidoids while combining with soil ampholitoids which will carry a positive charge, at a pH value below their isoelectric point, and act as basoids. Such combining is pronounced in red soils, yet, this type of phosphate adsorption should be regarded as chemical.

It is quite logical that, if the argillaceous minerals constituting the inorganic portion of the soil are capable of adsorbing and exchanging phosphoric acid anions in large amounts, then the soil itself must be capable for such exchange. By using the method of displacement of the phosphoric acid, fixed in the soil through adsorption, by ammonium fluoride (0.03 *N*) dissolved in hydrochloric acid (0.1 *N*), Markovsky established in experiments with some soils occurring in the Soviet Union that a sizable amount of phosphate ions is exchangeably adsorbed by them from the applied phosphorus fertilizers. Even after prolonged interaction between soluble phosphate and soils, the Dieckmann-Bray reagent extracts up to 70 per cent of the introduced phosphoric acid, 30 to 75 per cent of this amount being adsorbed exchangeably. However, in the course of time, chemical fixation starts being predominant.

A major role has been played by the tracer method. As was shown by Zamyatina (1954), introduction of ^{32}P-labelled phosphate into cultivated soddy podsolic soil initiates rapid isotope exchange. Already after an hour, this exchange is completed by 80 per cent, 25 per cent of the inorganic soil-derived phosphorus compounds becoming labelled after this period of time with 89 per cent of them being exchangeably adsorbed. The results of this experiment suggest that the isotope exchange involves primarily the mobile portion of the soil-derived phosphorus, which has been fixed by way of adsorption.

Klechkovsky has established that not only in neutral chernozem but also in acidic podsolic and red soils most of the introduced phosphoric acid anions are fixed in an exchangeable form and that these ions may be again displaced into the soil solution after the soil is treated with a salt solution.

Serdobolsky has provided proof of exchange adsorption of phosphate ions in the ordinary chernozem of the Kamen-

naya Steppe and podsolized loam from Dolgoprudny; however, red soil exhibits this capacity only to a minor extent. In the two above-mentioned soils, exchange adsorption ranged from 2-3 to 20-35 per cent of the introduced phosphorus, depending on the experimental conditions (doses of up to 200 mg P_2O_5 per 100 g of soil were tested). It has been noted that exchange adsorption from concentrated solutions was more pronounced.

Thus, the fact that phosphate anions undergo exchange adsorption in soils is beyond any doubt. This is extremely important for plant nutrition since, in terms of their availability to cultivated crops, adsorbed phosphoric acid ions have been experimentally demonstrated to be similar to water-soluble phosphates. However, soils contain very little water-soluble phosphates, and without uptake of the phosphoric acid anions adsorbed in the soil plant nutrition would have been inadequate for the normal growth and high yields of crops. It should be remembered that bicarbonate and organic acid anions effectively displace into solution the phosphate anions adsorbed by the solid phase of the soil. Desorption of the exchangeable phosphoric acid anions in soils (including peaty ones) is most complete in the presence of HCO_3^-, citric, and oxalic acid anions as well as sodium humates.

If there is one reason why the ability of plants to be sustained by phosphate ions adsorbed in the soil is without doubt, it is the constant release of carbon dioxide via roots (by way of respiration), which is dissolved in water and forms carbonic acid dissociating into H^+ and HCO_3^- ions; it is the latter that is exchanged for $H_2PO_4^-$ by soil colloids. Furthermore, plants are also characterized by exosmosis of organic acids (malic, citric, etc.). The soil itself has been found to contain little soluble humic substances whose constituent humic and other acids may be adsorbed in the soil as well, with displacement of phosphates into solution. Organic and inorganic acids also form in the soil as a result of decomposition of root and crop residues, incorporated organic fertilizers, and other substances by microorganisms. Hence, if the soil lacks anything, it is not phosphate desorbing agents, which is precisely why phosphates are so readily available to plants.

However, because exchangeable phosphate ions in the soil eventually become chemically fixed, phosphorus fertilizers must be applied in such a manner as to maintain them available as long as possible (water-soluble state, exchange adsorption). The exchange adsorption of phosphates by sesquioxides is less permanent than that by argillaceous minerals. Since hydrates of sesquioxides tend to pass from an amorphous to crystalline state, the adsorption of phosphoric acid by them decreases with increasing chemical fixation; this transition is more pronounced in the case of aluminium hydroxide, as opposed to ferric hydroxide. Soluble silicates, on the contrary, make phosphates more mobile:

$$K_2SiO_3 + CaHPO_4 = CaSiO_3 + K_2HPO_4$$

6.5 Phosphate Uptake by Plants and Yield Removal of Phosphorus

Experiments have shown that plants have become adapted to take up nutrients from extremely diluted solutions. Irrespective of the crops tested, the minimum concentration of P_2O_5 at which maize, oat, wheat, pea, mustard, and buckwheat could still take up this nutrient was 0.01 to 0.03 mg/litre.

Obviously, a crop can satisfy its demand in phosphorus only when such a solution is present in a rather large volume, and that is precisely what is often lacking in fields. If it is assumed that a hectare of topsoil weighs 3 thousand tons and its water capacity is 50 per cent (further assuming that all of this water is available to roots, which is impossible in reality), then, with a P_2O_5 concentration of 0.03 mg/litre, its total amount in such a layer will only be 45 g. If we also assume that the moisture content in the soil will remain the same throughout the vegetation period and the phosphorus content will be renewed a hundred times, we shall have only 4.5 kg P_2O_5 per hectare. Yet even an average yield of grain crops requires at least 20 kg P_2O_5 per hectare. This is why, at a 0.03-0.17 mg/litre concentration of P_2O_5 in the external solution, the coefficient of its concentration in plants must be as high as 4967 to 5520, respectively.

An excessively high concentration of phosphorus in the external solution is not desirable either. When grown on

water cultures, 20-day-old oat sprouts not only did not take up phosphorus, but also released the previously absorbed phosphorus if its concentration in the nutrient solution was in excess of 5 mg/litre (11.45 mg P_2O_5).

It has long been noticed that farm crops take up phosphates during the initial period of growth at a faster rate than at later stages. A plant builds up a reserve of this nutrient, then redistributes it among its organs depending on their phosphate requirements for synthesis of organic substances (constituent and reserve ones). Even complete elimination of phosphorus from the nutrient solution in physiological experiments with barley after five weeks of growth did not produce any adverse effect either on its yield or quality of the grain. Formation of the latter was enabled by migration of phosphates from vegetative into reproductive organs. In a similar experiment with spring wheat, elimination of phosphorus from its nutrition immediately after heading did not harm the plants in any way.

However, all crops are extremely sensitive to phosphate deficiency at the earliest age when the uptaking capacity of their underdeveloped root system is negligibly low. As has been found in experiments conducted at the agrochemical department of the Timiryazev Agricultural Academy in Moscow, if wheat is allowed to develop at the early age without phosphorus fertilizer and receives it later (after tillering), this results (when compared to normal phosphate nutrition) not only in a low yield of kernels, but also a decreased protein content in them with a sharp increase in that of inorganic (unassimilated) phosphates both in straw and in kernels. Phosphate deficiency delays the formation of organic acids from carbohydrates, which inhibits fixation of the ammonia nitrogen arriving through roots. Hence, phosphorus deficiency leads to incomplete utilization of nitrogen and other nutrients by plants.

Phosphorus deficiency at the early stage of growth depresses the plants to such an extent that even resumption of normal nutrition is not able to restore them completely. Moreover, when hungry in the beginning of their development, crops react negatively to subsequent ample supply of phosphates, which was observed on cotton grown in Uzbekistan.

Even large-seed crops (maize, cotton) deplete their phosphorus reserves soon after sprouting, and if this nutrient is not easily available after addition together with fertilizer at seeding and the soil contains only water-insoluble phosphates, sprouts may slow down their growth or even display signs of phosphate hunger. Cotton completely uses up its phosphorus reserves in seeds within the first ten to twenty days of growth, while maize does the same within the first two weeks. It is precisely during this period that they exhibit manifestations of phosphate deficiency even despite the ample reserves of available phosphorus in the soil. Symptoms of phosphorus hunger do not appear if the soil contains a small amount of readily available phosphate incorporated with fertilizer at seeding not far from the seeds. To this end, a little pelletized superphosphate is usually placed in the soil when maize is planted (7.5-10 kg P_2O_5 per hectare, 15 kg/ha for other crops, and 20 kg/ha for potatoes).

The P_2O_5 content in the tissues of maize plants is typically 0.30 to 0.35 per cent; if it drops to 0.20 per cent, the plants turn purple which, together with stunted growth, is a manifestation of phosphate deficiency; at later stages of development, a delay in ripening occurs.

The need of being additionally supplied with readily available phosphorus may be even more acute for small-seed crops with their modest phosphate reserves usually inadequate for vigorous growth. Experiments with tracers have made it possible to draw a quantitative distinction between phosphorus uptake from labelled fertilizers and from the soil (Tables 6.4 and 6.5).

As can be seen from Table 6.4, before young wheat plants become about four weeks old, they take up more phosphorus

Table 6.4. Uptake of Phosphorus by Wheat from Fertilizer and Soil

Source of phosphorus	Phosphorus uptake (mg per plant)			
	Age (weeks)			
	2	4	6	8
$NH_4H_2^{32}PO_4$	0.24	1.15	2.11	2.36
Soil	0.06	0.69	3.25	6.27

Table 6.5. Uptake of P_2O_5 by Oat from Superphosphate (^{32}P) and Soil (^{31}P) at Different Development Stages

Source of phosphorus	Growth stages			
	tillering	shooting	panicle formation	maturation
	mg of P_2O_5 taken up per plant			
Soil	0.30	1.74	3.25	3.65
% of the total	20.70	41.70	48.20	56.20
Fertilizer	1.15	2.44	3.50	2.84
% of the total	79.30	58.30	51.80	43.80

from the fertilizer and only later (when the root system is developed) from the soil. The tabulated data also permit calculating the rate of phosphorus accumulation by wheat: between the second and fourth weeks, the P_2O_5 content in the plant increased 6.1-fold, between the fourth and sixth weeks, 3.2-fold, between the sixth and eighth weeks, 1.7-fold. Hence, the P_2O_5 accumulation rate diminishes with the plant age.

In the experiment with oat (Table 6.5), the plants were allowed to mature. It can be clearly seen that the role of the soil in supplying oat with phosphorus increases with age.

Experiments with labelled phosphorus have revealed a high speed of phosphate translocation both from the soil into the plant and internally. It is a hundred and more times greater than the possible diffusion and osmosis rates.

Tracer experiments also convincingly testify to the uneven distribution of the absorbed phosphorus among the plant organs and tissues. The actively growing cells of the meristematic tissue of roots and leaves receive it in amounts hundreds and even thousands of times greater as compared to the plant parts in which cell division has already ceased.

A developing plant supplies large amounts of phosphorus to young leaves, and if its influx from the soil has stopped, the transport of phosphates from older into younger leaves is intensified. Because of this pronounced reutilization of phosphorus, experimenters must take older rather than young leaves to determine its content.

Within the first ten days, young maize plants take up easily available phosphates primarily from the root layer about a millimetre thick, the thickness of this layer increasing during the next hundred days to about 5 mm. Of particular importance is the total concentration of the soil solution, hence, its osmotic pressure: the higher the latter, the lower the phosphorus uptake rate. It was time and again observed that plants accumulate more phosphorus through ammonium rather than nitrate nutrition.

At the stages of formation and especially maturation of reproductive organs, phosphates are found to migrate extensively to the latter from the vegetative parts of the plant (from straw and leaves into the ear, from branches and stem into fruits, etc.) (Table 6.6).

Table 6.6. Distribution of P_2O_5 in Maize (% dw)

Growth stage	Internodes (from down upwards)					Tassel	Ear	Cob	Kernel
	1	3	5	7	9				
Tasseling	0.407	0.498	0.672	0.820	0.815	1.91	—	—	—
Full ripeness	0.076	0.124	0.158	0.225	0.239	—	0.644	0.017	0.664

As can be inferred from the tabulated data, the P_2O_5 content in the stem of maize increases from down upwards, that is, from the first to the ninth internode. At the ripening stage, the vegetative organs become markedly deficient in phosphates which are accumulated in the ear. At the tasseling stage, most of phosphorus is in the tassel and, during ripening, in the kernels.

Fibre flax takes up a maximum amount of phosphorus at the flowering stage; wheat does the same between the shooting and heading stages; the maximum uptake of phosphorus by potatoes is in July; sugar beet takes up the greater amount of phosphorus into its leaves, while its transport into the root is protracted in duration (the decrease in the P_2O_5 content in tops by the end of the vegetation period can be explained by their gradual dying away when the root still

continues to grow); cotton takes up nine tenths of its phosphorus after flowering.

Knowledge of the dynamics of phosphorus uptake by a particular crop permits taking appropriate measures to make sure that this nutrient is not deficient in the course of vegetation.

Although the absolute phosphorus content in plants over a given area, say one hectare, continues to increase till the crop becomes fully mature, the percentage content of this nutrient steadily decreases with plant growth.

A decrease in the relative phosphorus content in a crop means a more rapid accumulation of organic matter in which the previously taken amount of phosphorus and that being taken up at a slower rate at later stages are distributed. This, however, applies to the entire organic mass of the crop, without distinction between edible and inedible parts. We have already mentioned the translocation of phosphorus from vegetative into reproductive organs at the seed formation stage. This is why a decrease in the relative phosphorus content in seeds during their ripening is not as pronounced as in straw (Table 6.7).

Table 6.7. P_2O_5 Content (% dw) in the Kernels and Straw of Barley in Different Periods

Analysis date	P_2O_5 content	
	in kernels	in straw
May 29	—	0.85
June 17	1.05	0.56
July 3	0.90	0.35
July 27	0.96	0.17

Thus, phosphorus, just as nitrogen, is accumulated in the commercially valuable (edible) part of crops, which should be always remembered when applying phosphorus fertilizers. Usually, only a small portion of the valuable part of crops is put to direct use at the farm. The inedible part remains almost in its entirety on its territory, most of it

being used as fodder or litter for farm animals and eventually finds its way into the soil as part of manure. However, manure cannot return to the soil the nitrogen and phosphates removed from it by the valuable part of the crop, which is usually sold outside. And since the main task of socialist agriculture, expressed in most general terms, is to maximize the increase in commercial produce, any soil sooner or later reaches a point at which yields cannot increase steadily without incorporation of nitrogen and phosphorus with fertilizers.

In calculating the phosphorus balance at a farm, written on its debit side must be not only removal by the valuable part of the crop, but also that with livestock products. Every litre of milk sold by a collective or state farm includes an average of 0.9 g P_2O_5. A hundred dairy cows, each producing 5000 kg of milk, remove phosphorus in such an amount that the farm must place at least seven tons of 20% superphosphate in the soil to compensate for the loss. But this is not all if it is borne in mind that within the first two years crops take up phosphorus in an amount equal to 25 to 30 per cent of what has been placed with the fertilizer. Hence, complete and meaningful compensation will be achieved only if the quantity of the phosphorus incorporated with the fertilizer exceeds the amount removed with livestock products by a factor of three or four.

The phosphorus nutrition of plants must be maintained at the desired level to meet the requirements not only of crop production, but also of animal husbandry. A low phosphate content in the fodder makes it inferior so that inorganic phosphates must be added to cattle feed.

Fortunately, phosphorus is almost never lost through leaching from the soil into groundwater (in contrast to the tangible losses of nitrogen, sulphur, calcium, and other nutrients).

As has been shown by more than a hundred years of observations at the Rothamstead experimental station, experiments carried out in the Soviet Union and other countries, there is virtually no leaching of phosphates from heavy soils, although light soils do lose small amounts in this way. Even systematic application of phosphorus fertilizers enriching the arable layer of a loamy soil with phosphates has

almost no effect on the phosphate content in the subsurface horizons.

An approximate rate of phosphorus uptake by plants is most convenient to express in kilograms of P_2O_5 per centner of the commercially valuable part of the crop. However, since no grain can be grown without straw or taproots without tops, account must also be taken of the phosphorus assimilated by the useless part of the crop that corresponds to a centner of the valuable portion. General estimates for some crops are listed in Table 6.8.

Table 6.8. Phosphorus Content in Crops

Crop	Valuable part of the crop	P_2O_5 removal (in kg) per centner of commercial crop with due account for the inedible parts
Winter rye, oat, barley	Grain	about 1.0
Winter wheat	Ditto	1-1.35
Spring wheat	Ditto	1-1.2
Maize	Ditto	0.7-0.9
Pea	Ditto	about 1.55
Sunflower	Seeds	up to 2.6
Fibre flax	Fibre	about 2.6
Hemp	Ditto	up to 6.2
Cotton	Ditto	up to 1.5
Cucumber	Fruits	up to 0.14
Tobacco	Leaves	about 1.5
Tomato	Fruits	up to 0.11
Sugar beet	Roots	up to 0.18
Cabbage	Heads	about 0.10
Potato	Tubers	up to 0.15
Onion	Bulbs	up to 0.12
Red clover	Hay	about 0.55
Tea (green)	Leaves	0.4-0.5

It should be emphasized that the tabulated figures represent what is known as crop removal of phosphorus.

The effect of phosphorus on crops is in many respects opposite to that of nitrogen. Normal phosphorus nutrition accelerates the development of crops to some extent, causing them to mature earlier.

Phosphorus fertilizers increase the frost, drought, and lodging resistance of crops. Of particular importance is the

improvement of crop quality by phosphates. The percentage of grain increases faster than that of straw in the overall yield. Also improved is the chemical composition of crops: the content of proteins, sugars, and starch increases in grain and vegetable crops. In fibre crops supplied with sufficient amounts of available phosphorus, the fibre becomes stronger, longer, and finer.

The negative effects of excess phosphates in plants include premature ripening, which cuts down the quantity of commercial produce and leads to accumulation of excessively high amounts of inorganic phosphates in crops, which are not used in synthetic reactions, as well as early wilting of leaves.

6.6 Phosphorus Content and Forms in Soils

The phosphorus content in the Earth's crust is 0.12 weight per cent or about 1×10^{15} tons.

Phosphorus reserves in noncultivated soils depend on its content in the parent rock for lack of an alternative source. The situation is different when soils receive phosphorus fertilizers which are far from being fully utilized by plants. This is responsible for gradual accumulation of available phosphates in the arable layer of cultivated soils. If the average phosphorus content in the soil (0-20 cm) is taken equal to 0.4 per cent, then the soil continuum of the Earth will contain 1×10^{10} tons of this element. The phosphorus concentration in the soil solution varies from 0.1 to 1 mg/litre, the last concentration being much less common.

Crystalline igneous rocks contain about 0.275% P_2O_5, although the sedimentary rocks resulting from their disintegration, transportation by water and precipitation from it, and serving as the major source of soils, contain an average of 0.14% P_2O_5. The phosphorus content in arenaceous rocks amounts to only hundredths of a per cent. Consequently, over the aeons of geological evolution, phosphorus had been lost in the course of sedimentation. It precipitated from water in the form of nodules or strata containing phosphorite, whereas such an igneous phosphorus-rich mineral as apatite underwent disintegration and partially remained in the soil-forming parent rocks.

The soil-forming process involves gradual transfer of phosphates by the root system from lower to upper horizons. Therefore, the overall P_2O_5 content in the soil usually decreases sharply with depth. Yet this natural process of enrichment of the topsoil with phosphates is not sufficient to satisfy the requirements of farm crops giving high yields and cultivated for years.

Every soil contains inorganic and organic compounds of phosphoric acid with predominance of inorganic phosphates. This can be seen from the following relative indicators. If the total P_2O_5 content is taken as 100 per cent, then inorganic phosphates in the arable layer will account for 73 per cent in a highly podsolized loamy soil, 69 per cent in a moderately podsolized soil, 56 per cent in grey forest soil, 65 per cent in deep chernozem, 75 per cent in chestnut soil, and 86 per cent in sierozem.

In a soil reacting neutral, the bulk of inorganic phosphates is represented by fine-grained apatite. Acid soils contain predominantly iron and aluminium phosphates which are less readily available to plants than the phosphorus of apatites. However, liming of acid soils turns some phosphates of sesquioxides to calcium phosphates, which is beneficial for phosphorus nutrition of plants. The soluble phosphates introduced into the acidic soil after it has been limed are more readily available than those incorporated before liming.

Organic phosphorus compounds of the soil are present in the humus (anywhere from 0.8 to 2.5% P_2O_5 by weight depending on the soil type, the highest content being in grey forest soils) and phytates; calcium and magnesium phytates (phytins) being predominant in neutral soils, while aluminium and iron phytates prevail in acid soils. Phytates account for half the organic phosphorus in soils. Organic phosphates constitute from 14 per cent in sierozems to 44 per cent in grey forest soils of the total soil-derived phosphorus. The rest of the soils occupy an intermediate position. The higher the humus content in a soil, the richer it is in organic phosphates. Organic phosphates are mineralized by various microbes in the soil. Soil-derived phosphorus (just as nitrogen) is partially present in microorganism bodies, although this part is small. Even when each gram of soil contains five billion bacteria, the amount of the P_2O_5 fixed

by them throughout the arable layer does not exceed 24 kg per hectare. According to calculations, microorganisms account for 0.5-1% dw of the humus in podsolic soils and sierozems deficient in organic matter. Even in humus-rich chernozems this figure is much smaller, about 0.1 per cent.

In the soil layer immediately adjacent to the root system (rhizosphere) of alfalfa grown on irrigated sierozems of Central Asia, the population of bacteria may reach 20 billion per hectare. Then, in 100 g of such soil the P_2O_5 content in the microbial mass approaches 3.2 mg. Yet the soil layer constituting the rhizosphere accounts for only a minor portion of the entire soil in the root layer.

It should be pointed out that the phosphates present in the microbial plasma cannot play any significant role in the nutrition of higher plants until the microorganisms die away after their living conditions become adverse. Phosphorus will be always transferred to the next generations after division of mother cells. This was corroborated in experiments in which paramecia were labelled with ^{32}P and it was established that 16 offsprings of a cell lost in the fourth generation only 3.9 per cent of the phosphorus previously contained in the mother cell.

Phosphates of all univalent cations (of any degree of substitution) are readily soluble in water and, therefore, easily taken up by the root system. The same applies to monocalcium and monomagnesium phosphates, dihydrate $CaHPO_4 \cdot 2H_2O$ being much more soluble than anhydrous $CaHPO_4$. However, because of the rapid adsorption of phosphoric acid anions in the soil both chemically (formation of water-insoluble salts) and exchangeably (by positively charged soil colloids), the soil contains extremely small amounts of water-soluble phosphorus compounds, often less than 1 mg/kg of dry soil. This is not sufficient for adequate phosphorus nutrition of most crops and not because roots are not capable of absorbing phosphate ions from highly dilute solutions.

With 1 mg P_2O_5 being present in a kilogram of soil, a hectare of the topsoil (0-20 cm) will contain only 3 kg (the weight of the arable layer is usually taken equal to 3 million kg/ha), an average yield of cereals removing at least 20 kg P_2O_5 per hectare (much more in the case of industrial crops). These figures suggest that the available reserves of

water-soluble phosphates in the soil are not enough to ensure the average yield even if they are replenished several times throughout the vegetation period from the soil.

However, plants take up not only water-soluble phosphates, but also those soluble in weak acids, the latter (carbonic and such organic acids as citric and malic) being exuded by roots. It is they that dissolve some of the soil-derived phosphates insoluble in water. Much larger amounts of acids are released into the soil by microorganisms (nitric acid as a result of nitrification, sulphuric acid on oxidation of the reduced sulphur of proteins and amino acids, phosphoric acid in the course of mineralization of organic substances containing it). In addition, microorganisms release carbonic and organic acids as a result of respiration and metabolism.

Weak acids (or weak solutions of strong acids) dissolve disubstituted phosphates of bivalent cations (calcium and magnesium), thereby rendering them available to plants. Their conversion to a soluble form is promoted by carbonic acid, which is the most widely occurring acid in the soil.

Trisubstituted phosphates of bivalent cations are not soluble in water and poorly soluble in weak acids. Therefore, they cannot serve as sources of phosphorus for most crops with the notable exception of lupine, buckwheat, mustard, and, to a lesser extent, pea, hemp, sweetclover, and sainfoin, which take up phosphorus from trisubstituted phosphates and phosphorites. The special position occupied by the above crops stems from their two properties: intensive release of acids via roots and predominance of calcium over phosphorus in their composition. Both factors are responsible for more complete breakdown of the difficultly soluble phosphates eventually passing into more readily soluble salts which are then absorbed by the root system.

Soils with sufficient potential acidity (at least 2-2.5 meq/100 g) may adequately supply nutrients from the incorporated phosphorite to other plants as well. In such cases, however, the phosphorite is dissolved by the soil rather than root exudates.

Interestingly, if the currently prevailing concepts are to be believed, soils lack conditions appropriate for formation of tricalcium phosphate. It is more likely that even

less soluble compounds, such as octacalcium phosphate, $Ca_4H(PO_4)_3 \cdot 3H_2O$, and even hydroxyapatite, $Ca_5(OH)(PO_4)_3$, may emerge. Acid soils may give rise to phosphates of sesquioxides, which are then transformed into strengite, $Fe(OH)_2 \cdot H_2PO_4$, and variscite, $Al(OH)_2 \cdot H_2PO_4$. The solubility of iron and aluminium phosphates is minimum at pH 2.2 and 3.7, respectively, while that of tricalcium and trimagnesium phosphates is the lowest at pH 6.5 and 10, respectively. Thus, it is not surprising that a weakly acidic reaction of the soil (pH $\sim$ 6) is most favourable for phosphorus nutrition of plants. The reducing environment prevailing in peat bogs at a certain depth may lead to accumulation of ferrous phosphate known as vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, which is readily available to plants.

When the phosphorus-poor organic matter undergoes mineralization in the soil, the content of readily soluble inorganic phosphates may not only remain the same, but also go down. Ivanov was the first to notice that as early as 1905. In his experiments with composting of such substances (rich in cellulose) to which sodium phosphate was added (especially in combination with ammonium sulphate), complete disappearance of inorganic phosphorus was observed. As was established later, if the organic matter mineralized in the soil contains less than 0.2-0.3% P_2O_5, no release of available phosphorus compounds takes place at all; they are completely fixed by microorganisms.

The rate of organic phosphate uptake by plants from the soil increases to a certain point with its temperature, which is definitely a result of intensified microbiological decomposition of the humus and other organics. Experiments have shown that, when vegetative pots are immersed into baths at 20 and 35 °C, inorganic phosphates are taken up more vigorously at the former temperature, while organic phosphates, at the latter.

The soil has been found to host bacteria partially decomposing poorly soluble inorganic phosphates and converting them into more easily soluble ones. This process is also promoted by chemical reactions associated with the release of acids into the soil, both by roots and by microbes.

Estimation of Availabitity of Soil-Derived Phosphorus. In most soils, there are very little readily available phos-

phates. For example, in the deep chernozem of the Voronezh Region, containing 0.144% P_2O_5 (4230 t/ha of the arable layer), phosphates soluble in 2% acetic acid accounted for only 21 kg/ha. The podsolic loamy soil of the Moscow Region, containing 0.146% P_2O_5 (4380 t/ha of the arable layer), was found to have only 6 kg of acetic acid-soluble P_2O_5 per hectare. These data indicate that it is difficult to achieve a satisfactory yield on both types of soil, especially on the podsolic one, without applying phosphorus fertilizers, which has been supported by practice.

The most readily available to plants are water-soluble phosphates, but there is usually so little of them in soils that their content cannot, as a rule, serve as a reliable indicator of the degree of phosphorus supply to plants. This, however, does not mean at all that the presence of these salts in the soil should be disregarded. It has already been mentioned that all plants are capable of taking up phosphorus from highly dilute solutions. And since there is a certain equilibrium between the solid phase and soil solution, the water-soluble phosphates absorbed by roots are gradually brought back to the previous low level, and plants can take them up again. Unfortunately, most soils are deficient in this source of phosphorus and, when phosphorus fertilizers are not applied, cultivated crops suffer from phosphate hunger or, at any rate, from lack of phosphorus for a decent yield.

In determining the degree of phosphorus supply to crops, it has become very important to take weakly acidic extracts from the soil, permitting retrieval from the latter not only of water-soluble phosphates, but also those that are not soluble in water yet constitute reserves of available phosphorus. The following acids are used for extraction: 1-2% citric acid, 2-3% acetic acid, 0.2 *N* hydrochloric acid, and 0.002 *N* sulphuric acid (with addition of ammonium sulphate to maintain the pH value at a constant level of about 3); another good reagent for extraction of available phosphates from the soil is carbonated distilled water.

A general characteristic of all laboratory methods for determining available phosphorus in the soil is that they provide relative indicators that are meaningful only in the context of a valid field experiment involving a certain type of soil occupied by the same crop.

The rapidity, low cost, and sufficient accuracy of soil analysis for available phosphates using chemical methods have made it a valuable tool for agrochemical services which combine it with field experiments. The results of chemical analyses are recorded in the form of charts and recommendations to collective and state farms.

Coming back to chemical methods, we should like to point out that citric acid extracts iron phosphates, which are abundant in acid podsolic soils. In this respect, acetic acid is more suitable for determining available phosphates in acid soils than citric acid.

The content of available phosphates is a dynamic indicator, varying as a function of soil properties, cropping intensity, and other factors. Consider, as an illustration, the results of analysis of two samples of cultivated soddy podsolic soil at the experimental station of the Timiryazev Agricultural Academy (Table 6.9).

Table 6.9. P_2O_5 Content in Various Extracts

Soil sample	P_2O_5 content in mg per 100 g of air-dry soil extracted with		
	carbonated distilled water	0.5 *N* acetic acid	0.5 *N* hydrochloric acid
1	0.77	2.87	15.00
2	1.87	6.20	63.10

The analytical results indicate that the second soil is richer in phosphates. Now, the question arises as to their content in a hectare of topsoil. This can be easily calculated: 1 mg P_2O_5 per 100 g corresponds to 30 kg in a hectare of a 0-20 cm thick soil layer. Then, the answer is: 22.1 kg of available P_2O_5 per hectare of the first soil, and 56.1 kg/ha for the second soil.

Plants do not take up all of the available phosphates present in the soil for a number of reasons, one being the inability of the root system to cover the entire surface of soil particles, totalling tens of thousands of square metres per hectare. Hence, the first soil contains too little available phosphates to ensure a satisfactory yield.

The reagents listed in Table 6.9 have been recommended by Chirikov (1947) who contended that carbonated distilled water dissolves soil-derived phosphates of alkaline cations (of all degrees of substitution), mono- and disubstituted phosphates of calcium and magnesium, and, partially, trisubstituted phosphates of these two cations (trimagnesium phosphate being more soluble). The salts passing into this solvent are taken up by plants more readily.

The second reagent extracts tricalcium phosphate, partially phosphorite, apatite, aluminium phosphates, alcohol and sugar phosphates. These compounds cannot be classified as readily available to all crops. Although their content in both soils is much higher than that of phosphates extractable with carbonated distilled water, the analytical results must be evaluated with a greater degree of caution. Comparison with the results of field experimentation has shown that if 0.5 *N* acetic acid solution extracts less than 5 mg P_2O_5 per 100 g of soil, plants are not adequately supplied with phosphorus. This gives every reason to believe that the first soil does not contain enough available phosphates for normal yields, and phosphorus fertilizers will have to be applied at an increased rate. On the other hand, the second soil contains a moderate amount of available phosphorus, and the fertilizers may be applied moderately. Only when an acetic acid extract contains more than 10 mg P_2O_5 per 100 g, the soil is said to have enough available phosphates for crops.

As regards the third group of phosphates passing into a 0.5 *N* hydrochloric acid solution, they cannot be considered as available and include phosphorite, apatite, aluminium and iron phosphates, and phytates. Determination of phosphates of the third group is of no practical value. All its results tell about their reserves that can eventually give available phosphates.

The amounts of mobile P_2O_5 in soils, determined by different methods, give an indication of what is known as the phosphorus capacity of a soil but not its phosphate potential. This potential decreases when P_2O_5 is taken up by plants and increases when the soil is fallowed or receives a phosphorus fertilizer.

6.7 Commercial Phosphorus Fertilizers

6.7.1 Raw Materials for Phosphorus Fertilizer Production

Of the numerous minerals containing phosphorus only the igneous apatite and sedimentary phosphorites may serve as raw materials for the phosphorus fertilizer industry.

Apatite is an igneous mineral widely occurring in a dispersed state in parent rocks that have given rise to soils. Yet its deposits are scarce. The largest deposit was discovered in 1925 in the mountain massif of Khibiny on the Kola Peninsula. Less important and valuable apatite deposits occur in the Urals, in the south of the Baikal area, in Brazil, Spain, Canada, the United States, and Sweden.

Phosphorites have formed as a result of mineralization of the skeletons of animals inhabiting the Earth in the remote geological past and also precipitation of phosphoric acid from water through the agency of calcium.

Phosphorite deposits occur widely, but those in Western Europe are small and not suitable for mining. Almost no such deposits are found in Asian countries with the exception of China (Yunnan). Major phosphorite deposits occur in some countries of North Africa. On the American continent, they have been found in Florida, Tennessee, and other states.

Unfortunately, most of our phosphorites contain little phosphorus, being abundant in sesquioxides instead, which makes them difficult to process into superphosphate. A valuable phosphorite deposit was discovered in the Soviet Union in 1937, in the Karatau Mountains (Southern Kazakhstan); it is relatively close to the areas of intensive application of phosphorus fertilizers, namely, Central Asian republics specializing in irrigated cultivation of cotton. Other major deposits of phosphorites occur in the Kingisepp District of the Leningrad Region and in the Estonian SSR.

While apatite is crystalline, phosphorites may be both amorphous and crystalline. Amorphous phosphorites are more prone to decomposition and are, therefore, of particular interest for direct application without chemical processing.

In spite of the different origins of apatites and phosphorites, there is a lot of common in their chemical structure. They are essentially tricalcium orthophosphates with small

amounts of calcium fluoride, other calcium compounds, and various impurities. Apatite crystals are characterized by high strength; chemical or thermal removal of fluorine breaks down the crystal lattice of apatite.

The empirical formula of apatite is $Ca_5(PO_4)_3F$ or $[Ca_3(PO_4)_2]_3 \cdot CaF_2$; calcium fluoride may be substituted by calcium chloride, carbonate, or hydroxide. Accordingly, distinction is made between fluorapatite, chlorapatite, carbonate-apatite, and hydroxyapatite.

Apart from phosphate minerals, phosphorites contain many impurities: sesquioxides, sand, and clay. The Khibiny apatite occurs as an apatite-nephelite rock known as nepheline, which is an aluminosilicate with the composition $(K, Na)_2O \cdot Al_2O_3 \cdot 2SiO_2 + nSiO_2$. Phosphorites may be of concretionary type (which is more frequent), in the form of pebbles, and (less frequently) in the form of solid rock. The Karatau phosphorite belongs to the latter type: it forms beds 7 m thick as opposed to 0.8-1.5 m in other deposits. It is superior in quality with respect to other phosphorites, containing 29.6-35.6% P_2O_5 and only 2.-2.5% sesquioxides (as opposed to 4-11% in other deposits). However, the Karatau phosphorite has one drawback: it contains too much magnesium, which renders its processing difficult. The product is usually highly hygroscopic, and special techniques must be used to resolve this problem. Other deposits contain less phosphorus and more sesquioxides.

Deposit	Percentage content of	
	P_2O_5	$Al_2O_3 + Fe_2O_3$
Aktyubinsk	about 18	3.4
Vyatka-Kama	23-27	5-10
Egor'evsk	16-25	5-6 and more
Krolevets	about 18	3.5
Shchigry	16-17	3.5

The phosphorus content is higher in land (clayey) phosphorites, including those from the Vyatka-Kama, Egor'evsk, Kineshma, and Krolevets deposits. Sandy phosphorites, with the exception of glauconite ones, contain less phosphorus and are mined near Donetsk, Morshansk, and Seshchensky. Glauconite is an alumoferrisilicate of the composition $K_2O \cdot 4R_2O_3 \cdot 10SiO_2 \cdot nH_2O$ with up to 8% potash. Glauconite phosphorites contain 1-4% potassium; in terms of

phosphorus, they occupy an intermediate position between clayey and sandy phosphorites.

Sesquioxides are not desirable in raw phosphates because they call for greater quantities of acid to be used in processing and cause retrogradation of soluble phosphates (their transition to a less soluble form). An excellent raw material for phosphorus fertilizers is provided by the Khibiny deposit of apatites. Finely ground rock is roiled in water with addition of a reagent, namely, oleic acid with kerosene and soluble glass (1 kg per kg of rock). Air is blasted through the pulp, whereby apatite particles float up and coalesce, while nepheline settles down and is carried away with the water stream. The apatite concentrate separated from nepheline contains 39-40% P_2O_5 and is considered to be the best starting material for production of soluble phosphorus fertilizers. Nepheline also finds practical uses. It is applied as a potassium fertilizer to acid soils.

The total amount of phosphorus in the known deposits of apatite and phosphorite around the world is as high as 1×10^9 tons, but only a small portion is of commercial value. At the present rate of phosphate mining, which is in excess of 28 million tons of P_2O_5 a year, raw phosphates would last 3 thousand years. It should be borne in mind, however, that this rate has been steadily increasing, and the extraction techniques undergoing improvements. The most promising in this respect is the thermal process yielding elemental phosphorus and highly concentrated polyphosphates on its basis. Predominant today is the wet process (treatment of apatite or phosphorite with sulphuric acid or its mixtures with nitric or phosphoric acid). Disadvantages of the wet-process phosphoric acid include its contamination and that of its end product with numerous impurities, and a low concentration of the derived fertilizers. Another promising process involves production of elemental (red) phosphorus which, when copper oxide is added to it (1% of phosphorus weight), is gradually oxidized in the soil to orthophosphoric acid (H_3PO_4) readily available to plants*. Of course, elemental phosphorus lacks dead weight and lends itself ideally to transportation (229% P_2O_5).

* Testing of pyritic slag to this end, as suggested by Peterburgsky, has been successful.

6.8 Processing, Composition, Properties, and Application of Phosphorus Fertilizers

All types of phosphorus fertilizers that are calcium phosphates are divided into three groups: (1) monosubstituted water-soluble; (2) disubstituted semisoluble (insoluble in water but soluble in weak acids and, therefore, available); and (3) trisubstituted water-insoluble and poorly soluble in weak acids, unavailable for the overwhelming majority of crops if not decomposable by soil acidity to give more readily soluble salts. Processing of raw phosphates has for its aim their conversion into an available form.

The most widely used group of phosphorus fertilizers around the world is the first one including superphosphate.

6.8.1 Monosubstituted Phosphates

Superphosphate. Treatment of finely ground phosphate rock with sulphuric acid of the right concentration (57% and higher) gives a mixture of monocalcium phosphate and anhydrous calcium sulphate with hydrogen fluoride volatilizing and being trapped:

$$[Ca_3(PO_4)_2]_3 \cdot CaF_2 + 7H_2SO_4 + 3H_2O = \\ = 3Ca(H_2PO_4)_2 \cdot H_2O + 7CaSO_4 + 2HF$$

A ton of the raw material requires about a ton of acid to yield up to two tons of the end product. Consequently, the phosphorus content in the fertilizer is about half as low as in the starting material. This is the main reason why low-percentage phosphorites are not suitable for processing into superphosphate. Processed from apatite concentrate is superphosphate containing at least 19% citric acid-soluble P_2O_5, the top grade containing even 19.5% P_2O_5. The product of processing of the Karatau phosphorite contains only 14% available P_2O_5.

In addition to the main reaction, i.e. that between tricalcium phosphate and sulphuric acid, other reactions occur. For example, in those portions of the reaction volume where inadequate mixing leads to excess of sulphuric acid, tricalcium phosphate decomposes completely, yielding phos-

phoric acid, calcium sulphate, and hydrogen fluoride:

$$[Ca_3(PO_4)_2]_3 \cdot CaF_2 + 10H_2SO_4 = 6H_3PO_4 + 10CaSO_4 \downarrow + 2HF$$

Because of this reaction, phosphoric acid is present in sizable amounts: 5 per cent in the top and first grades and up to 5.5 per cent in the Karatau product. Phosphoric acid is responsible for high acidity of superphosphate and its hygroscopicity (according to the standard, the moisture content in the fertilizer should not exceed 12-15%). To eliminate acidity, superphosphate is neutralized with ammonia, lime, or phosphorite.

Naturally, in the places where incomplete mixing leads to sulphuric acid deficiency, dicalcium phosphate (precipitate) is formed, which is available by virtue of its solubility in weak acids:

$$[Ca_3(PO_4)_2]_3 \cdot CaF_2 + 4H_2SO_4 + 12H_2O = 6CaHPO_4 \cdot 2H_2O + 4CaSO_4 + 2HF$$

Thus, superphosphate includes the following available compounds: monocalcium phosphate, dicalcium phosphate, and free phosphoric acid. The monophosphate and phosphoric acid account together for 75 to 90% P_2O_5. Hence, the diphosphate accounts for a maximum of 25-10% P_2O_5 (available). A small amount of tricalcium phosphate remains undecomposed, whereas phosphoric acid partially combines with iron and aluminium (1% iron oxide combines with 2% P_2O_5, while 1% aluminium oxide combines with 1% P_2O_5). The free phosphoric acid in superphosphate prevents formation of gypsum ($CaSO_4 \cdot 2H_2O$), therefore, calcium sulphate remains anhydrous or combines with only one water molecule for every two $CaSO_4$ molecules. It constitutes up to 40 mass % of the fertilizer.

Powdered superphosphate is dark grey (if derived from phosphorite) or light grey (if derived from apatite) and has the specific odour of phosphoric acid. When applied to neutral base-saturated soils, the monophosphate is converted into dicalcium phosphate with relative ease:

$$Ca(H_2PO_4)_2 + Ca(HCO_3)_2 = 2CaHPO_4 \cdot 2H_2O + 2CO_2$$

In the presence of carbonates, the conversion partially goes on:

$$Ca(H_2PO_4)_2 + 2Ca(HCO_3)_2 = Ca_3(PO_4)_2 + 4H_2O + 4CO_2$$

Under these conditions, hydroxy- and fluorapatite may even emrege in the soil. The chemical absorption of phosphoric acid and superphosphate in neutral soils with formation of dicalcium and tricalcium phosphates is responsible for the low mobility of the phosphorus from the incorporated fertilizer. At the same time, freshly precipitated tricalcium phosphates are characterized by good solubility in weak acids and availability to plants. In acid soils rich in sesquioxides, poorly soluble and, therefore, almost unavailable iron and aluminium phosphates may form:

$$Ca(H_2PO_4)_2 + 2Al(OH)_3 = 2AlPO_4 + Ca(OH)_2 + 4H_2O$$

In all soils, part of the phosphoric acid anions are adsorbed by positively charged colloidal particles (in exchange for other anions, primarily HCO_3^-), and it remains available in this state. Soil microorganisms also fix a certain amount of phosphates by translocating them into the cell plasma.

To minimize the chemical absorption of phosphate ions from powdered superphosphate, it should not be mixed with large amounts of soil. If this precaution is taken, less phosphates will pass into the unavailable state. The first evidence to prove this was supplied in experiments with local application of superphosphate.

Chemical fixation of superphosphate phosphorus is minimized through reduction of the area of its contact with the soil, which is achieved by granulating or pelletizing fertilizers.

Pelletized Superphosphate. This form of fertilizer is easily obtained by slightly moistening the powdered product and drying it in a rotary drum. As a result, pellets of different sizes are produced. Those ranging from 1 to 4 mm in diameter are considered to be of the right size. Larger pellets are crushed and, together with the smaller ones, sent for repelletizing (recycling) with a new batch of the powdered product. The recycle stock provides sites for formation of new pellets. Being more expensive than powdered superphosphate, the pelletized product is, on the other hand, much more effective, particularly when placed near seeds at sowing, and near transplants and tubers at planting. This is the most rational use of pelletized superphosphate.

Note that, when applied locally, it is as effective as three times the same amount of powdered superphosphate spread evenly before ploughing or tillage; in both cases, we are speaking of equal areas under treatment. Pelletized superphosphate is produced from the best stock; it contains less moisture (1-4%) and is characterized by a higher content of available P_2O_5 (19.5-22% versus 14-19.5% in the powder), lower acidity (1-2.5% versus 5-5.5%), and better physical properties, which provides for improved drillability of the fertilizer. However, as a result of neutralization, the content of water-soluble P_2O_5 decreases. With appropriate precautions being taken, it may even be applied mixed with seeds.

Concentrated Superphosphate (double and triple). The fact that ordinary superphosphate contains 40 % $CaSO_4$ makes it unsuitable for transportation. It would be wrong to assume that gypsum is merely ballast, or dead weight, for all soils and crops. In the case of gypsum-treated alkaline soils as well as soddy podsolic soils and especially sandy loam with typically low contents of sulphates and sulphur in general, all fertilizers containing sulphate ions are more effective than those lacking them. For some crops, such as legumes and cruciferae, with increased sulphur uptake, gypsum in superphosphate may be beneficial. Yet for most other soils and crops gypsum is almost useless. Hence the desire to get rid of it in producing superphosphate.

The process of manufacturing concentrated superphosphates comprises two steps. First, phosphorite (even low-analysis one) is treated with an acid to extract free phosphoric acid. (The reaction with sulphuric acid at a higher acid-to-phosphorite ratio as compared to production of ordinary superphosphate was described above, see page 326.) Then, after filtering H_3PO_4 off gypsum, a new batch of high-analysis phosphate stock is treated with it; the result is concentrated superphosphate, that is, monocalcium phosphate with a small amount of impurities present in the stock:

$$[Ca_3(PO_4)_2]_3 \cdot CaF_2 + 14H_3PO_4 + 10H_2O = 10Ca(H_2PO_4)_2 \cdot H_2O + 2HF$$

This is what is known as the wet process of phosphoric acid production.

An improved process for producing phosphoric acid has been developed and is being introduced—sublimation, or dry distillation, of phosphorus from low-analysis phosphorites at temperatures ranging from 1400 to 1600 °C in electric or blast furnaces with coke or anthracite. The released elemental phosphorus is collected under water, then burnt in the presence of air, and the resulting phosphorus pentoxide is made to combine with water: $P_2O_5 + 3H_2O = 2H_3PO_4$.

The phosphoric acid produced in this fashion may be used in the manufacture of not only concentrated superphosphate, but also other valuable fertilizers. As far back as the forties, apatite concentrate was treated with phosphoric acid in Kirovsk (Khibiny) to yield superphosphate containing 50% P_2O_5 in an available (as well as water-soluble) form.

Ordinary and concentrated superphosphates, taken in equivalent quantities in terms of phosphorus, are equally effective insofar as crop yields are concerned. Therefore, the advantages of the concentrated fertilizer boil down to lower expenditures involved in packaging, transportation, storage, and application.

For local application it is preferable to use concentrated superphosphate in pelletized form.

Treatment of apatite concentrate with a mixture of sulphuric and phosphoric acids yields enriched superphosphate containing 23.5-24.5% available P_2O_5. It is applied in the same manner as other varieties of this fertilizer.

In order to determine the content of available P_2O_5 in superphosphate, two extracts are taken from its sample, one with water and the other with alkaline solution of ammonium citrate; the latter reagent dissolves dicalcium phosphate and, partially, aluminium and iron phosphates which are then erroneously regarded as available. Therefore, the richer the phosphate stocks in sesquioxides, the less reliable the results of this superphosphate determination method. In some countries, a neutral solution of ammonium citrate is used to determine available phosphoric acid in superphosphate. The trouble with this reagent is that it dissolves not only dicalcium but also tricalcium phosphate, although the latter does not belong to available salts. As can be inferred from the foregoing, the notion of "available" phosphorus is

rather arbitrary in the sense that being available to wheat and buckwheat, on the one hand, or hemp, lupine, and mustard, on the other, means two different things in view of the fact that the latter crops may also take up poorly soluble salts, something that cannot be expected of cereals.

6.8.2 Disubstituted Phosphates

Precipitate (precipitated calcium phosphate). We have already mentioned the availability of phosphorus from dicalcium and dimagnesium phosphates. Dicalcium phosphate has long gained worldwide acceptance, although to a much lesser extent than superphosphate. The reason is that superphosphate may be used as both local and basal fertilizer and even, if necessary, for dressing (in which case it must be incorporated into the soil to a sufficient depth).

Precipitate, on the contrary, is suitable primarily for basal application when it is spread evenly over the field surface then ploughed down to the necessary depth. A plant starts taking up the basal fertilizer phosphorus after it has developed a strong root sytem penetrating into the lower part of the topsoil. A locally applied fertilizer is, in contrast, a source of nutrients for young sprouts with still weak roots and, therefore, not yet capable of taking up poorly soluble salts.

When used as a basal fertilizer, precipitate is as effective on most soils as superphosphate. On acid soils, it may be even more effective than superphosphate because the latter tends to undergo retrogradation in such soils and is more fully converted into phosphates of sesquioxides, as compared to precipitate. Precipitate is produced by neutralization of phosphoric acid with milk of lime (a suspension of calcium hydroxide):

$$H_3PO_4 + Ca(OH)_2 = CaHPO_4 \cdot 2H_2O$$

Depending on the quality of the starting material, the P_2O_5 content in precipitate ranges from 25-27 to 30-35 per cent. It is soluble in ammonium citrate and available to plants. This fertilizer is applied at the same rates as superphosphate. Precipitate exhibits good physical properties: it does not cake and is readily drillable. It is a white or

light grey powder. Precipitate is subjected to analysis for citrate-soluble P_2O_5 or, in other words, P_2O_5 extractable with an alkaline solution of ammonium citrate.

Defluorinated Phosphate. The superphosphate industry is a major consumer of sulphuric acid around the world, yet sulphur and pyrites, from which H_2SO_4 is produced, are becoming in short supply. This is why chemical engineers have been trying to develop an acid-free process of breaking down phosphorites and apatites in the manufacture of phosphorus fertilizers. Significant advances have been made in thermal treatment. In this respect, production of the so-called defluorinated phosphate is particularly promising.

The process resides in calcination of apatite (with addition of 2-3% silica) or the Karatau phosphorite (with addition of lime) at 1400 to 1450 °C in the presence of water vapour. Under such conditions, the crystal lattice of apatite disintegrates, and fluorine is removed by as much as 90 per cent. As a result, phosphorites of various composition, soluble in weak acids, are obtained. Treatment of apatite yields a fertilizer containing 30-32% P_2O_5, while that of phosphorite yields a product containing 20-22% P_2O_5; 70 to 92 per cent of these phosphates are soluble in 2% citric acid. It has been established that, when applied at equal rates in terms of P_2O_5, superphosphate and defluorinated phosphate are close in effectiveness. Defluorinated phosphate is also used as an inorganic additive to animal food deficient in P_2O_5.

Thomas Slag. This is a by-product of processing phosphorus-rich iron ores. The essence of the Thomas process is as follows. Burnt limestone is added into the converter where the metal is melted. It enters into a reaction with the phosphoric anhydride resulting from the melting to yield tetracalcium phosphate $4CaO \cdot P_2O_5$ (or $Ca_4P_2O_9$). The slag rises to the surface and, after separation and cooling, is ground. In addition to tetracalcium phosphate, the product also contains poorly soluble phosphates of no value to plant nutrition. Furthermore, the fertilizer is rich in calcium silicate and contains compounds of iron, aluminium, vanadium, magnesium, manganese, molybdenum, and other nutrients, including micronutrients. Application of this fertilizer leads to a decrease in micronutrient requirement. The composition

of Thomas slag may vary widely. The lack of uniformity in its composition is also evident from the citric-soluble P_2O_5 varying from 7-8 to 16-20 per cent. Thomas slag is a dark heavy powder used only for basal application. Its effectiveness is higher on acid soils because of its alkaline reaction.

Thomas slag, Bessemer slag, and defluorinated phosphate are analysed for P_2O_5 soluble in 2% citric acid, this form of phosphates is usually referred to as citric-soluble. Passing into solution are monocalcium and tetracalcium phosphates as well as silicophosphates present in Thomas slag, Bessemer slag, and other thermophosphates ($Ca_5P_2 \cdot SiO_{12}$ or $Ca_4P_2O_9 \cdot CaSiO_3$).

Open-Hearth Slag. In the production of steel from cast iron in the open-hearth process, lime is also added to bind phosphorus. The by-product is a slag poorer in phosphorus than Thomas slag, known as open-hearth or furnace slag. It contains a double salt of tetracalcium phosphate and calcium silicate, iron, manganese, magnesium, and other components. The P_2O_5 content varies from 8 to 12 per cent. It is almost completely soluble in citric acid. The reaction of the fertilizer is highly alkaline. Because of its low nutrient content, open-hearth slag is used near its sources; it is most suitable for acid and weakly acidic soils. Open-hearth slag is used only for basal application. Sugar beet is highly responsive to it.

6.8.3 Trisubstituted Phosphates

Ground Phosphate Rock. This fertilizer is obtained by grinding phosphorite to a fine powder. Phosphorus is present in the form of hydroxyapatite, carbonate-apatite, fluorapatite, and $Ca_3(PO_4)_2$. These compounds are insoluble in water and weak acids. Their availability to plants is minimal. The soil starts breaking down phosphorite at a potential acidity of at least 2.5 meq/100 g of soil. The higher this value, the more effective the ground phosphate rock, provided the content of mobile phosphates in the soil is not sufficient for nutrition of crops. It is also important to take into consideration the overall absorbing capacity of the soil ($T = S + H$ meq/100 g), which will permit establishing the extent to which the nonsaturation of the soil with bases is

manifest, that is, the percentage of *H* in the capacity of a given soil to exchangeably adsorb cations. Another factor of interest is base saturation of the soil. If its value is below 70, the probability of effectiveness of ground phosphate rock is rather high. Ground phosphate rock should be applied when there is a certainty that this will be of benefit. This is an important consideration in view of the fact that in the zone of acidic podsolic and soddy podsolic soils one may encounter fields and plots where phosphorite is not effective because of the insufficiently high level of potential acidity or for other reasons (e.g. high degree of base saturation or high content of available phosphates).

As early as the turn of the century, experiments carried out by Engelgardt demonstrated the importance of ground phosphate rock as a fertilizer for podsolic soils.

Pryanishnikov calculated that ground phosphate rock can be applied in the Soviet Union at high rates over an area of 80 million hectares. This alone attests to the enormous economic potential of the fertilizer in this country.

Pryanishnikov's experiments in which he studied the effect of phosphorite species and properties on the soil when applied as fertilizer have shown amorphous phosphorites that can be easily broken down to be more effective than crystalline ones. Of particular importance is the fineness of the fertilizer; the smaller its particles, the greater their specific surface, and hence, the more intimate the contact with soil colloids carrying hydrogen ions on their surface. The acids present in the soil solution, too, interact more readily with the tiniest particles of ground phosphate rock, making the constituent phosphates soluble. Years of experimentation at the Dolgoprudny agrochemical station have shown that, when applied at the same rate (45 kg P_2O_5 per hectare), finely ground phosphorite produces almost the same effect on the yields of winter rye as superphosphate (Table 6.10).

Another finding made at Pryanishnikov's laboratory was the importance of concomitant fertilizers in rendering phosphorite more readily available: physiologically acidic fertilizers (ammonia salts and, to a lesser extent, potassium ones, excluding ash, cement kiln dust, and nepheline) promote decomposition of ground phosphate rock in the soil; on the contrary, physiologically alkaline fertilizers (nitrates)

Table 6.10. Effect of Phosphorite Fineness on Winter Rye Yield

Yield increase	Due to superphosphate	Due to ground phosphorite (with particle size, mm)		
		0.08	0.08-0.17	0.17-0.5
In cent/ha	4.1	3.6	2.9	1.8
In %	26	23	18	12

slightly mitigate this process. Liming of soils prior to phosphoric application is not desirable because lime neutralizes the acidity of the soil solution and the most mobile part of potential (exchange) acidity of the soil's solid phase, whereby the interaction of phosphorite with the soil is restricted and protracted in time. Observations have shown that, when phosphorite contains calcium carbonate, its trisubstituted phosphate is not broken down by the soil until lime carbonate dissolves. However, after ground phosphorite has been applied and its reaction with the soil has occurred partially, moderate liming of acid soils can be done. It should be borne in mind that phosphorite cannot substitute for liming at economically acceptable rates. Therefore, as acidity inhibits the growth of plants on highly acidic soils, it renders them incapable of taking up the phosphates that have passed into soluble compounds as a result of interaction between ground phosphate rock and the soil.

At the Dolgoprudny agrochemical station, changes in the forms of soil acidity and the degree of its base saturation were insignificant even ten years after ground phosphate rock had been applied liberally, although most of it had decomposed by that time (Table 6.11).

If it is borne in mind that rates exceeding 90-135 kg P_2O_5 in phosphorite are not practical, then the insignificant changes in soil acidity caused by this fertilizer become understood.

Phosphorite is broken down completely by acid peat. As has been established at Pryanishnikov's laboratory, at a high ratio of highland peat to phosphorite (100 : 1), the phosphates of the latter convert completely into water-soluble compounds. However, there is no need to break down phosphorite completely. It is quite sufficient to convert it

Table 6.11. Effect of Increasing Ground Phosphate Rock Rates on Soil Properties

Soil property	P_2O_5 rate (kg/ha) in ground phosphate rock				
	0	45	135	270	540
pH of the water extract	5.7	5.5	5.6	5.8	5.8
Potential acidity (meq/100 g of soil):					
exchange	0.42	0.41	0.25	0.16	0.16
hydrolytic	2.93	2.95	2.78	2.58	2.50
Degree of base saturation (%)	66	68	75	78	79

into dicalcium phosphate, which is why peat-phosphorite composts may be prepared with a peat-to-phosphorite ratio of 95 : 5 or 90 : 10. Such composts may be mixed using not only high but also low peat which often exhibits sufficiently high potential acidity to break down phosphorite, to say nothing of its being much richer in ash and ash elements than high peat.

Pryanishnikov's experiments have also shown that different plants respond differently to application of ground phosphate rock. Most crops can use it only at an appropriate soil acidity. They include cereals, flax, sugar beet, potatoes, pea, clover, and vetch. Among these, winter rye, clover, and pea assimilate this fertilizer better than others. Another group of crops may assimilate ground phosphorite at a weakly acidic and even neutral reaction. This group includes lupine, buckwheat, sainfoin, and mustard. These crops are also characterized by increased uptake of phosphorus from the soil.

Ground phosphate rock ranks first among phosphorus fertilizers in duration of its positive effect on yields. Hence, there is no need to phosphatize acid and weakly acidic soils more than once per cycle of even the longest crop rotation period. On the other hand, superphosphate must be applied at seeding to fertilize all crops. Such a combination of insoluble and soluble fertilizers takes care of both

economy and complete satisfaction of plants. What remains to be done is only making sure that crops receive adequate amounts of other nutrients (nitrogen, potassium) whose deficiency cannot be rectified by phosphorus alone. In many cases, some micronutrients may be deficient, too.

The total P_2O_5 content in ground phosphate rock must be 25 per cent in the top grade, 22 per cent in the first grade and 19 per cent in the second grade; the moisture content must not exceed three per cent irrespective of grade; the fineness expressed in terms of the percentage of particlees retained on a sieve with 0.18 mm mesh should not exceed 20.

6.9 Application of Phosphorus Fertilizers

6.9.1 Starter Application of Superphosphate

At present, the phosphorus balance in the soils of the USSR is positive on the average (about 20 kg P_2O_5 are applied with inorganic and organic fertilizers per hectare, which exceeds its average yield removal). However, in most regions some crops remove more phosphorus from the soil than it receives with fertilizers. Cotton, sugar beet, potatoes, flax, tea, and some other industrial crops are better in this respect. The average positive balance indicators are due to increased phosphorus rates in the Non-Black Earth zone of the European part of the USSR, including the RSFSR, the Baltic republics, Belorussia, and North Ukraine (Polesye).

In North Kazakhstan, Western Siberia, and in the southeast of the European part of the RSFSR, the phosphorus balance remains negative. Crop yields in these regions remove at least 80 per cent of soil-derived phosphorus.

Drilling of pelletized superphosphate in a mixture with seeds increased winter grain crop yields by 3 centners per hectare (averaged over 169 experiments). Spring wheat yields (averaged over 89 experiments) increased after the same treatment by 2.3 cent/ha. The drilling technique is also important. For example, when labelled pelletized superphosphate is placed at a distance longer than 5 cm from oat or buckwheat seeds, the uptake of phosphate ions by sprouts is slowed down. Larger fertilizer pellets are also

responsible for a slower uptake of locally applied phosphorus by young plants.

The rate of P_2O_5 to be applied at seeding depends on the crop and equals 7.5 to 20 kg/ha. All crops are responsive to this superphosphate application technique but some of them are strongly inhibited when seeds are in direct contact with the fertilizer (maize, sunflower, cotton). Therefore, they must be separated by a soil layer, and phosphorus rates may be minimal (7.5-10 kg/ha).

Grain cereals are less sensitive and respond positively to pelletized superphosphate even when it is mixed with seeds before being placed by an ordinary drill (about 10 kg P_2O_5 per hectare). A similar response is displayed by flax, hemp, and vegetables. When sugar beet is seeded by a combined drill or potato tubers are planted by a potato planter, up to 20 kg P_2O_5 are applied with pelletized superphosphate (mixed with nitrogen and sometimes nitrogen and potassium fertilizers).

When seeding and application of pelletized superphosphate are done by a drill, the following conditions must be met: the seeds and fertilizer must be dry (to prevent dissolution of superphosphate components and their effect on the seeds before they reach the soil), the pellets must be strong enough not to be broken in the seeding mechanism and clog it, and, finally, superphosphate must be neutral or weakly acidic.

Even after a brief contact with seeds (2 hours), acid superphosphate reduces the germination rate of winter rye, barley, spring wheat, flax, and table beet. When the fertilizer acidity is minimum (1%), it may be mixed with rye and beet seeds at least two hours before seeding or four to eight hours in advance in the case of the other above-mentioned crops. Neutralized superphosphate may be mixed with seeds of the above crops 24 hours before the mixture is placed. Each phosphate pellet 1.5 mm and larger in diameter creates an area of increased phosphate concentration in the soil for young plants. It has been established that two months after incorporation of pelletized superphosphate into the soil such areas retain anywhere from 20-25 to 68-83 per cent of the applied phosphorus in an available form; the former figures refer to red soils and the latter, to cherno-

zems, soddy podsolic soils occupying an intermediate position.

Having summarized the results of experiments with pelletized superphosphate, research workers concluded that 15 kg P_2O_5 in pelletized superphosphate placed in the row provide for the same increase in the yield of various crops as 45 kg P_2O_5 per hectare in broadcast powdered superphosphate. High and stable yields of all crops cannot be achieved without application of the basal fertilizer always used at a higher rate and ploughed down.

6.9.2 Basal Application of Phosphorus Fertilizers

If local application of superphosphate is aimed at intensifying the initial growth of plants, the basal fertilizer has for its aim to eliminate phosphorus deficiency so that crops could be supplied with it throughout most of the vegetation period. This deficiency stems from the fact that transition of phosphates in the natural soil reserves from unavailable to available form is influenced by a number of factors so that it proceeds extremely slowly and insufficiently.

The factors determining basal application include: (1) application time; (2) depth of placement; (3) form (solubility); (4) rate; and (5) combination with other nutrients.

For soils with a reaction close to neutral, the time of application of soluble phosphates is immaterial because they are not lost through leaching and the chemical fixation is restricted to formation of dicalcium phosphate which is available to plants. Application of superphosphate into chernozem 557 days before seeding did not reduce its effect on the yield of crops with different physiological characteristics (maize, oat, millet, clover).

In addition to dicalcium phosphate, aluminium and iron phosphates also appear in acid soils, their availability to plants being minimal. Hence, one should avoid prolonged interaction between superphosphate and acid soils in the absence of plants.

Of paramount importance is the depth of placement of the basal phosphorus fertilizer in view of the fact that

phosphoric acid anions are far from being highly mobile in the soil.

Surface distribution of superphosphate on a pasture even at a high rate (450 kg P_2O_5 per hectare), in experiments with ^{32}P, prevented penetration of phosphorus deeper than 2.5 cm. As plants grow, the percentage of the phosphorus from fertilizers decreases. This was demonstrated, in particular, in an experiment with maize. When it was sown, superphosphate was incorporated to a depth 5 cm below seeds and at the same distance aside.

	Early development	Formation of tassel	Ripening
P_2O_5 amount taken from fertilizer (% of its total content in plants)	45-95	11-33	7-13

At the beginning of growth, all of the phosphorus present in the plants was taken up from the fertilizer, and by the ripening stage it only accounted for about 0.1, while 0.9 was taken up from the soil. Even in a greenhouse experiment, when the root system goes through the entire soil volume, the depth of phosphorus placement affects significantly the availability of the nutrient. Only when placed to a depth of 10 cm and more was the effect of the fertilizer predominant in phosphate nutrition.

In the field, the depth of placement of the basal phosphorus fertilizer is even more important as regards its uptake by plants, especially in a zone of insufficient humidity. Both water and nutrients are taken up by plants via root hairs, however, the latter do not develop in a dry soil or soon die away in it. And it is precisely the upper part of the arable layer that is desiccated several times within a summer even in a zone of sufficient humidity. During such periods, phosphorus fertilizers placed to a shallow depth will not be available to roots. The role of deep placement of superphosphate was emphasized by Timiryazev who experimented in the Simbirsk Province in the dry year of 1867. He noticed that superphosphate enhances the resistance of grain crops to drought. This finding was time and again corroborated by other scientists.

Even in irrigated soils the mobility of phosphates is insignificant: as was demonstrated by four years of observations in Virginia (USA), when applied on the surface at a rate of 112 to 224 kg P_2O_5 per hectare of silt-loam soil, phosphate ions from superphosphate covered a distance of only 5 cm. Without irrigation, water-soluble potassium and calcium phosphates in heavy soils penetrated to a depth of 0.5 to 1.5 cm, and only in light soils their penetration was deeper. Fertilizers placed to a small depth are mixed with a thicker layer during reploughing. This, however, produces a positive effect only on the subsequent crops, while the farm would like to see a phosphorus induced increase in the yields of the crop treated with the fertilizer, which is impossible if superphosphate has been placed to a shallow depth (e.g. by harrowing). The depth of ploughing for a given crop determines the depth of placement of the basal phosphorus fertilizer. Its rates depend on soil fertility, the estimated yield of the first crop, the precursor, and concomitant fertilizers, varying from 30-45 to 90-120 kg P_2O_5 per hectare. High rates are typically applied to fruit and industrial crops, especially on infertile soils; moderate rates are applied to maize, potatoes, vegetable and fodder crops; lower rates are applied to grain cereals and pulses.

It has been found that the fertilizer phosphorus utilization factor is 5 to 15 per cent and, under favourable conditions, even as high as 25 per cent. A higher utilization factor—21 to 40 per cent—occurs on meadows and pastures.

One of the ways of enhancing the uptake of fertilizer phosphorus by crops is to create its reserves in the soil.

The effectiveness of phosphorus fertilizers increases considerably when they are applied locally (Table 6.12).

The effect of the precursor manifests itself primarily on the nitrogen supply to the crop under treatment. The crops planted after legumes, which leave a certain amount of nitrogen in the soil assimilated by nodule bacteria from the atmosphere, respond better to phosphorus than those planted after other precursors (Table 6.13).

Evaluation of various forms of phosphorus fertilizers used for basal application is necessary to select the best in agrotechnical and economic terms for particular soil conditions

Table 6.12. Effect of Localised Application of Phosphorus Fertilizers on the Phosphorus Utilization Factor (data supplied by the Byelorussian) Academy of Agricultural Sciences)

Crops	Yield increases due to $N_{60}P_{60}K_{60}$ (cent/ha)		Calculated phosphorus utilization factor (%) (1st year)	
	broadcasting	application	broadcasting	application
Potato	119.0	166.0	29.3	50.2
Winter wheat	7.1	11.9	13.7	23.1
Winter rye	4.4	7.4	9.4	14.1
Oat	5.7	8.8	8.2	13.8

Table 6.13. Effectiveness of Superphosphate in Crop Rotation with Clover at Equal P_2O_5 Rates

Crop	Yield increase (cent/ha) in crop rotation	
	without clover	with clover
Winter rye	1.1	6.2
Ditto	1.5	3.5
Sugar beet	30.8	66.6

and crops. In the Soviet Union, the main phosphorus fertilizer is superphosphate.

Yield increases due to superphosphate are similar on all soils except for grey forest soils and southern chernozems where they are much lower. The lower response of crops to superphosphate on grey forest soils stems from the higher mobility of organic phosphorus compounds in them and a poorer nitrogen supply to crops, as compared to chernozems. On southern chernozems, the culprit is insufficient moisture.

In experiments aimed at determining the effect of equal P_2O_5 rates in ordinary and concentrated superphosphate as well as precipitate, increases in the yields of various crops on soddy podsolic soils, grey forest soils, degraded, deep and ordinary chernozems were found to be very much the same.

As has already been mentioned, the effectiveness of ground phosphate rock depends on soil acidity, crop, and other factors. In the USSR, about 4 million tons of ground phosphate rock are currently used. If it is applied at optimal and scientifically substantiated rates, i.e. 3 to 4 centners per hectare, one can fertilize 10 to 12 million hectares of phosphorus-deficient soddy podsolic soils.

The great variety of soils in the Soviet Union permits all types of phosphorus fertilizers to be used successfully.

In order to avoid ammonia losses, alkaline forms of phosphorus fertilizers (Thomas slag, open hearth slag) should not be mixed with ammonium salts. Dry superphosphate may be mixed with dry ammonia and nitrate fertilizers shortly before application. Mixing with ammonium nitrate well in advance may lead to dampening of the mixture, while doing the same with ammonium sulphate may cause its hardening by the newly forming gypsum. Mixing acid superphosphate with nitrate fertilizers may entail losses of volatile nitric acid ($H_3PO_4 + NaNO_3 = NaH_2PO_4 + HNO_3$).

The acidity of superphosphate is harmful to plants, which is why it must be neutralized. To this end, up to 15% ground phosphate rock or up to 10% dolomitic meal, or the same amount of lime carbonate are added to superphosphate with stirring. Caustic lime should not be added to avoid conversion of phosphoric acid into poorly available compounds. As has been shown by many years of experimenting with superphosphate, soil acidity does not change when this fertilizer is applied.

Dampening adversely affects the physical properties and drillability of all phosphorus fertilizers; for example, superphosphate pellets lose shape. To prevent this, they must be stored dry in the manufacturer's packaging.

6.9.3 Dressing with Superphosphate

The need to dress crops with phosphates during their growth is prompted by the desire to compensate for the phosphorus deficiency, which can be detected from the crop appearance, as well as to make up for insufficient rates of the phosphates applied with the basal fertilizer and to

raise the P_2O_5 utilization factor on acid soils by cutting down the time of interaction between superphosphate and soil particles or even obviating this interaction (foliar dressing).

Phosphoric acid ions are taken up via leaves and not only are actively translocated into other plant parts, down to roots, but are also released by the latter into the soil. However, foliar phosphorus nutrition is of limited importance and does not give much in quantitative terms as far as the plants are concerned. Foliar dressing is difficult to carry out over large areas and expensive because of high water requirements stipulated by the need to repeat spraying with highly dilute solutions so as not to burn leaves.

Serious difficulties are also involved when superphosphate is used for soil dressing. Since phosphoric acid anions are fixed in the soil chemically and physicochemically at a relatively fast rate and almost completely, the migration of the fertilizer from the place of its incorporation is negligible in both vertical and horizontal directions. Hence, spreading superphosphate over the soil surface is not admissible if it cannot be followed at least by harrowing for its incorporation (flax and other close-growing crops).

It may so happen that for some or other reason farms fail to apply the basal fertilizer at a desired rate; then, dressing is inevitable.

The dressing of row crops with superphosphate during inter-row tillage and to a right depth (at least 10-12 cm, preferably 14-16 cm) is rather effective but only if the basal phosphorus fertilizer has been applied at an insufficient rate.

Experiments in which phosphorus was partially taken from the basal fertilizer to be used for dressing sugar beet have shown that such an approach is not advisable.

Chapter 7

Potassium Fertilizers

7.1 Potassium in the Life of Plants and Its Content in Crops

Three potassium isotopes are known to occur in nature: ^{39}K, ^{40}K, and ^{41}K, the second isotope being radioactive and having a half-life of 1.3×10^9 years. Radioactive ^{40}K accounts for about 0.01 per cent of natural potassium. Besides, a short-lived radioactive isotope of potassium, ^{42}K, is obtained artificially (half-life: 12.4 h).

Potassium is present in plants in an ionic form and is not a constituent of any organic compound in cells. It is found primarily in the cytoplasm and vacuoles but not in the nucleus. About 20 per cent of this nutrient are retained in plant cells in an exchangeable state by cytoplasmic colloids, up to one per cent is nonexchangeably absorbed by mitochondria, and the major portion (about 80%) is present in the cell sap and easily extractable by water. Therefore, potassium is washed out from plants by rains, especially from old leaves.

The potassium accumulating in chloroplasts and mitochondria stabilizes their structure and promotes formation of energy-rich ATP in the processes of photosynthetic and oxidative phosphorylation. In the light, the bond linking the potassium ion with cytoplasmic colloids becomes stronger, while in the dark it becomes weaker, and potassium is partially released from plants via roots.

The effect of potassium is pronounced primarily insofar as it intensifies the hydration of cytoplasmic colloids, increasing the degree of their dispersion, which enables plants to better retain water and withstand temporary droughts. Under the effect of potassium more starch is accumulated in potato tubers, while sugar beet accumulates more sucrose and some fruit and vegetable crops accumulate

more monosaccharides. Potassium enhances the cold endurance and winter hardiness of crops (by virtue of increased osmotic pressure of the cell sap) as well as their resistance to fungous and bacterial diseases.

Potassium intensifies the synthesis of high-molecular carbohydrates (cellulose, hemicellulose, and also pectins, xylans, etc.) with the result that the walls of cells in the straw of cereals become thicker and their resistance to lodging increases, while the quality of flax and hemp fibre improves; it also catalyzes the activity of some enzymes, promotes synthesis and accumulation of certain vitamins in plants (e.g. thiamin and riboflavin), and is essential for the activity of guard cells.

Potassium (just as calcium and magnesium) is also important for ammonium nutrition of farm crops. Potassium deficiency upsets plant metabolism. It also inhibits the activity of some enzymes, disrupts carbohydrate and protein metabolism in plants through increased expenditure of sugars in respiration, makes kernels sickly, reduces the germinating capacity and vitality of seeds, and, ultimately, impairs the crop quality. When the potassium supply to crops is not adequate, they are more prone to various diseases and, once harvested, more difficult to preserve in marketable condition.

The manifestations of potassium deficiency in plants are as follows: old leaves turn yellow prematurely, starting from the edges; later, their edges and apex turn brown (sometimes with red, rusty spots), then the edges undergo necrosis and disintegration so that in the end they look burnt and lacerated. Suffering most from potassium deficiency are potassium-loving plants.

Potassium deficiency slows down most of the biochemical processes associated with virtually every aspect of metabolism. This gives every reason to believe that all the observed irregularities stem primarily from potassium deficiency.

Potassium is taken up by plants in a cationic form, apparently remaining in the cell as a charged ion forming only weak bonds with cell substances. Being accumulated in sizable amounts in the cell, potassium serves as the main counterion for neutralization of the negative charges of

both inorganic anions and cell polyelectrolytes, as well as creates ionic asymmetry and a potential difference between the cell and external solution. This is possibly the specific function of potassium that makes it an indispensable inorganic nutrient for plants.

This characteristic of potassium was pointed out by Sabinin who wrote that the role of cations, i.e. potassium, sodium, and to some extent calcium, is restricted to their involvement in the formation of cytoplasmic structures and sustaining the electric properties of the boundary formations of the protoplast.

The significant increase in the membrane potential of the cell and its more pronounced dependence on metabolic processes, as well as the increased selective permeability of the cell membrane to potassium, represent one of the primary impacts of potassium deficiency. The changing potential gradient and flux of substances across cell membranes may be directly responsible for the many disturbances in plant metabolism when potassium is deficient.

It is known that the potassium content in the cell by far exceeds that of other cations in it as well as the potassium concentration in the external solution. For example, the intracellular concentration of potassium in higher plants exceeds that in the external solution a hundred to a thousand times.

Some experiments have revealed a close correlation between the potassium content in the cell and growth rate. For example, potassium deficiency seems to slow down the division, growth, and elongation of cells.

At present, there is ample evidence to the effect that the intensity of protein synthesis in plants is closely associated with their potassium content. Potassium deficiency makes photosynthesis less productive.

Lack of potassium has been found to slow down considerably the efflux of photosynthesis products from leaves. The critical period of potassium uptake by plants coincides with their early growth stages (within the first 15 days after sprouting). Plants usually take up most of the potassium they need during the period of intensive accretion of the biomass. In the case of cereals and pulses, the potassium

uptake is over by the flowering and milky ripeness stages, for flax, this happens at the peak of the flowering stage, and in the case of potatoes, sugar beet, and cabbage, the potassium uptake is extended in time, covering almost the entire vegetation period. Potatoes take up most of their potassium at the flowering and intensive tuber formation stages, sugar beet does so at the root formation stage, and cabbage, during head formation.

Potassium is necessary for incorporation of phosphate into organic compounds and also for the reaction of phosphate group transfer.

Potassium-activated enzymes control a great variety of reactions playing a major role in the above processes. For example, phosphofructokinase regulates glucolysis. Potassium also activates the enzymes involved in the formation of acetoacetyl coenzyme A.

Studies into the role of potassium in enzyme activation have shown that, as this cation interacts with the enzyme molecule, it may change the enzyme conformation, whereby an enzyme-K^+-substrate complex is formed. Potassium possibly serves as an ion-effector with respect to not only enzymic but also other proteins.

It has been established that cell membranes are more permeable to potassium than to other ions, with the exception of H^+.

A decrease in the potassium content in the cell is counterbalanced by an increase in that of sodium, magnesium, and calcium. In the case of potassium deficiency, the cell contains more free ammonia, hydrogen ions, and inorganic phosphates. There is evidence that the content of sulphates and nitrates also decreases.

Potassium is always more abundant in young growing organs of plants and also in the meristem and cambium. It is translocated from old leaves into younger ones, that is, it is reutilized in plants. The reutilization is more pronounced when potassium is deficient in the nutrient medium with the result that the lower leaves turn yellow earlier than during normal potassium nutrition.

The translocation of potassium from older into younger leaves is assisted by sodium which replaces it in the tissues and leaves that have ceased growing. Hence, the distribu-

tion of potassium in a plant is characterized by what is known as basipetal concentration gradient: its content in leaves and stem parts per unit dry weight increases from down upwards.

The content of potassium in plants, soils, and fertilizers is usually expressed in terms of its oxide, K_2O. The average potassium content in the products of some farm crops is given in Table 7.1. As compared to cereals and legumes, sugar beet, fodder beet, and potatoes contain much more potassium per unit dry weight of the main and by products. The potassium concentration is particularly high in the products of vegetable crops. Grain crops take up almost the same or a smaller amount of potassium as compared to nitrogen and two to three times more than phosphorus (the $N : P_2O_5 : K_2O$ ratio is 2-3 : 1 : 2-3.5). Vegetables, potatoes, sugar beet, and other root crops take up about one and half times more potassium than nitrogen and three to four and a half times more than phosphorus. Various crops remove different amounts of K_2O per 10 centners of the main product (with due account for the corresponding quantity of by-products): grain crops remove about 25 to 37 kg, pulses, 16 to 20 kg, potatoes, 7.0 to 9.0 kg, sugar and fodder beets, 6.7 to 7.5 kg, vegetables, 4.0 to 5.0 kg, clover and timothy (hay), 20 to 24 kg.

The removal of nutrients by various crops per unit main product with due account for the corresponding quantity of by-products (e.g. per 10 centners) does not always lend itself to comparison when used to represent the uptake of a particular nutrient by a given crop because of the different contents of dry matter in the yields of different crops. This is why it is preferable for a more objective comparison of nutrient removal by crops to express the yield of main products in terms of equivalent dry weight units. For instance, to yield 50 centners of dry weight of the main product per hectare requires the following amounts of potassium for various crops at an equivalent main product yield in terms of fresh weight:

Table 7.1. Average K_2O in the Products of Some Farm Crops (% dw)

Crop	Product	K_2O (%)	Crop	Product	K_2O (%)
Winter	Grain	0.65	Cabbage	Heads	4.60
cereals	Straw	1.10	Carrot	Roots	3.20
Spring	Grain	0.67	Cucumber	Fruits	5.65
cereals	Straw	1.30	Tomato	Ditto	5.60
Maize	Grain	0.43	Flax	Straw	1.10
	Forage	1.93	Cotton	Fibre	1.00
Pea	Seeds	1.46	Red clover	Hay	1.80
	Forage	0.60	Alfalfa	Ditto	1.80
Sugar beet	Roots	1.00	Vetch	Ditto	1.20
	Tops	3.00	Timothy	Ditto	2.42
Fodder beet	Roots	3.50			
	Tops	2.63			
Potato	Tubers	2.40			
	Haulm	3.70			

Crop	Yield capacity (cent/ha)	Yield removal K_2O (kg/ha)
Cereals	58	175
Potato	200	180
Sugar beet	200	150
Fodder beet	420	280
Clover, alfalfa (hay)	60	120
Cabbage	660	290
Table carrot	420	210
Sunflower (seeds)	55	990

As a rule, potatoes, sugar beet, fodder beet, and some vegetables yield more dry matter per hectare than, for example, cereals and grasses, and, therefore, they remove more potassium. Sunflower stands apart in that it takes up much more potassium than any other crop.

The removal of nutrients per unit main product yield is strongly dependent on the ratio of the commercially valuable to inedible portions of the crop. In the case of grain crops, the edible portion contains less potassium than the inedible one, while in root and tuber crops, perennial grasses, ensilage and vegetable crops, most of potassium is concentrated in the valuable portion. For example, wheat kernels contain only up to 15% potassium present in the above-ground part, the rest, or 85 per cent, being concentrat-

ed in straw. On the other hand, potato tubers contain at least 95% potassium, whereas the haulm accounts for only up to 5% of the total removal of this nutrient when the crop is harvested. The smaller the amount of potassium in the marketable portion of the crop, taken away from the farm, and the greater this amount in the inedible portion remaining in the field and also that used as fodder at the farm, the more potassium stays in the biological cycle and the better the balance of this nutrient in the soils of the farm.

As a result of partial shedding of plants, washing of potassium away from leaves by rains, and its being released into the soil via roots, the yield removal of K_2O is usually lower by the end of the vegetation period, as compared to its maximum content in the plants during their intensive development.

Soil-Derived Potassium. The overall reserves of potassium in the topsoil are 5 to 50 times greater than those of nitrogen and 8 to 40 times greater than those of phosphorus. Hence, soils, as a rule, contain much larger reserves of potassium than nitrogen and phosphorus. In soddy podsolic sandy loam potassium (K_2O) reserves amount to one or two per cent, in soddy podsolic loam, about two per cent, in grey forest soils and podsolized, leached, ordinary chernozems and sierozems, about 2.5 per cent, in southern chernozems and chestnut soils, about two per cent, in red soils, 0.6 to 0.9 per cent, and in alkaline soils, 1.2 to 3.0 per cent. There is very little potassium in peaty soils (0.03-1%). Small reserves of potassium are sometimes found in flood plain soils (0.3-2.2%) as well.

Potassium occupies primarily the inorganic portion of the soil, its content in the organic portion being extremely small. The soil-derived potassium is present in: (1) the crystal lattice of primary and secondary minerals (most of it); (2) colloidal particles, both in exchangeable and nonexchangeable states (a significant part); (3) afterharvesting and root residues as well as microorganisms; and (4) inorganic salts of the soil solution (carbonates, nitrates, chlorides, etc.), which is but a tiny fraction of the total potassium reserves.

The best source of plant nutrition is soluble potassium salts. Plants readily take up the potassium of afterharvest-

ing and root residues as well as microorganisms after they die away. A directly available reserve comprises exchangeable cations and poorly soluble salts. Next in importance come hydromicas, vermiculites, secondary chlorites, montmorillonite, nonexchangeable cations, and poorly soluble salts.

A potential reserve includes feldspars, micas, pyroxenes, and primary chlorides.

Total potassium includes various forms of potassium compounds that may be classified as follows: (1) water-soluble potassium (readily available to plants); (2) exchangeable potassium (readily available); (3) mobile potassium (water-soluble plus exchangeable potassium) removable from the soil with a salt extract; (4) non-exchangeable hydrolyzable potassium (poorly exchangeable or reserve) additionally extractable from the soil with an effervescent solution of a strong acid (usually 0.2 *N* or 10% HCl solution) and serving as the nearest nutrient reserve; (5) acid-soluble potassium combining all of the preceding four forms and extractable from the soil with an effervescent solution of a strong acid (0.2 *N* or 10% HCl); and (6) nonexchangeable potassium (difference between total and acid-soluble ones).

It should be clarified that exchangeable potassium and the nonexchangeable hydrolyzable one are determined by way of calculation: exchangeable potassium is determined from the difference between the mobile and water-soluble ones (since passing into a salt extract, in addition to exchangeable potassium, is also the water-soluble form), while nonexchangeable hydrolyzable potassium is determined from the difference between the acid-soluble and mobile ones.

The content of mobile potassium in the soil, which is the principal available form, constitutes only 0.5 to 2 per cent of the overall K_2O reserves. Hence, about 99 per cent are represented by the unavailable forms. Yet even these can be taken up by plants to some degree or another.

Experiments have shown that there is a mobile (dynamic) equilibrium between soil-derived potassium forms, and if, for example, a plant takes up water-soluble potassium, its amount in the solution is made up by the exchangeable one, whereas a decrease in the latter may after some time be compensated for by non-exchangeable, fixed potassium. Thus, as plants take up mobile potassium, its reserves

will be replenished by poorly exchangeable potassium and by that confined within the crystal lattice of minerals. According to some research workers, alternating desiccation and moistening of the soil, typical of field conditions, accelerate this process to some degree, the transition of potassium into available forms is also promoted by plants themselves. The different forms of potassium in various soils is as follows, according to some sources (mg K_2O per 100 g of soil):

Soil	Water-soluble	Exchangeable	Acid-soluble	Total
Soddy podsolic sand	1.8	6.5	26.0	1155
Heavy soddy podsolic loam	3.5	12.8	161.0	2840
Deep loamy chernozem	3.1	14.1	331.0	2380

Hence, soils contain about 10 to 25 per cent of the water-soluble form of potassium compounds, with respect to the exchangeable form, 5 to 25 per cent of the exchangeable form with respect to the acid-soluble one, and 2 to 15 per cent of acid-soluble potassium with respect to total potassium.

In agricultural chemistry, the reserves of soil-derived potassium for plant nutrition are usually expressed in terms of the content of its mobile form. For different soil types we have standard methods to determine mobile potassium: Kirsanov's method (0.2 *N* HCl extract) for the soddy podsolic and grey forest soils of the Non-Black Earth zone; Chirikov's method (0.5 *N* acetic acid extract) for non-calcareous chernozems; Machigin's method (1% ammonium carbonate extract) for calcareous chernozems, chestnut and brown soils, and sierozems; Oniani's method (0.1 *N* sulphuric acid extract) for the red and yellow soils of humid subtropical zones; and the Egner-Rime-Domingo method (a buffer solution of lactic and acetic acids plus ammonium acetate, pH 3.7) for soils in the Baltic republics. Widely used in the past and today has been Maslova's method (1.0 *N* ammonium acetate extract) applicable to soddy podsolic soils, grey forest soils, non-calcareous chernozems, and mountain non-calcareous soils. The results of soil analysis

are used to draw agrochemical charts showing the soils of a farm with their mobile potassium content. The highest content of mobile potassium is usually found in ordinary and southern chernozems as well as chestnut and brown soils. It is also abundant in typical, leached and podsolized chernozems, grey-brown, takyr-like soils, solonchaks, and sierozems. The least amounts of potassium are found in soddy podsolic sand and sandy loam, yellow, red, flood plain and, especially, peat-boggy soils.

A characteristic of the potassium regime of the soil must include not only quantitative determinations of mobile potassium, but also the degree of its mobility, hence, availability to plants. Methods have been developed to enable such an evaluation which is based on the physicochemical relationship between potassium, calcium, and magnesium ions in the "soil-soil solution" system and is expressed in terms of the thermodynamic potential of potassium, also known as the potassium potential, which is regarded as the soil-derived potassium "intensity factor". Taking into consideration that Ca^{2+} and Mg^{2+} cations in the absorbing complex of the soil exhibit similar exchange properties, the sum of activities of these ions is regarded as the activity of ions of the same species.

By potassium potential is understood a free energy change in exchange reactions between potassium cations, on the one hand, and calcium and magnesium cations, on the other, in the "solid phase-solution" system of the soil at constant temperature (25 °C) and pressure (1.01×10^5 Pa).

The potassium potential is given by the formula $\Delta Z^0 = pK - 0.5p\,Ca$, where p is the negative logarithm of activities of K^+ and $Ca^{2+} + Mg^{2+}$. This potential is determined in a soil suspension after a soil sample has been shaken in a 0.002 *M* solution of calcium chloride for 30 minutes (soil : solution = 1 : 2).

The activity of these ions is found using the formula $ai = Ci \cdot fi$, where ai is the ionic activity, Ci is the ionic concentration, and fi is the ionic activity coefficient calculated from the Debye-Huckel equation:

$$\log f = \frac{0.51 \cdot Zi^2 \sqrt{Y}}{1 + \sqrt{Y}},$$

where Zi is the ionic valence and Y is the ionic strength of the solution. The value of Y is found, in turn, using the formula

$$Y = 0.5\Sigma C_1 Zi^2,$$

where C_1 is the concentration of the ion of interest and Zi is its valence.

The potassium potential of the soil is indicative of the possibility of the potassium adsorbed in it passing into solution with due account for the competition of the accompanying bivalent cations. The greater the numerical value of the potassium potential, the lower the capacity of K^+ to pass into solution, hence, its availability to plants. Since the derived value is a negative logarithm, the potassium potential is a universal and relatively constant indicator for each soil type.

According to the commonly accepted gradation, the potassium potential value of 2.5 to 2.9 is indicative of potassium deficiency for normal development of plants, the value of 1.8 to 2.2 corresponds to optimal conditions, and values below 1.5 correspond to a relative excess of this nutrient. The potassium potential can to some extent be used for diagnosis of potassium nutrition of crops and to make recommendations as to fertilizer rates.

The supply of potassium to plants depends not only on the content of its mobile compounds in the soil and the potassium potential, but also on the capacity of the soil to maintain the latter at a constant level with varying content of mobile potassium in the soil, as a result of its removal by crops and application of fertilizers. This capacity of the soil was termed by Buckett *potential buffering capacity* of the soil with respect to potassium, or PBC^k.

The potential buffering capacity of the soil with respect to potassium is a ratio between two quantities: the capacity factor (Q), which implies the amount of directly available potassium (extractable from the soil with a 0.002 M solution of $CaCl_2$), and the intensity factor (I_0) which is essentially equilibrium activity of K^+ in the soil solution. The Q/I_0 ratio varies from one soil to another.

It has been experimentally demonstrated that the potassium potential values of 1.80 to 2.35 in grey forest soil

correspond to adequate supply of plants with this cation; at values ranging from 2.50 to 2.84, the potassium supply is not sufficient; and when the potassium potential reaches 3.27 to 3.54, crops suffer from acute potassium deficiency.

The potential buffering capacity of the soil with respect to potassium in a 0-20 cm layer reaches 45, and at a depth of 80 to 100 cm it is as high as 200, that is, there is little mobile potassium in the former case. A correlation was found to exist between changes in potassium activity and the uptake of this nutrient by plants.

7.2 Potassic Mineral Deposits. Production of Potassium Fertilizers and Their Properties

The Soviet Union ranks first in potassic mineral reserves and production of potassium fertilizers. For example, in 1978, the production of potassium fertilizers around the world was 25.7 million tons in terms of K_2O, including 8.4 million tons in the USSR. The application rates in the same year were 15.9 kg K_2O per hectare worldwide and 23.2 kg in the USSR. At present, the commercial reserves of potassium salts all over the world are estimated to be 50 billion tons K_2O, 48 per cent of this amount being in the Soviet Union.

The raw material for the production of potassium fertilizers is natural potassium salts whose commercial deposits in the USSR occur primarily in the European part, Kazakhstan, and Central Asia. The largest deposit is in the Upper Kama region (about 12 billion tons), near Solikamsk. All potassium salt deposits in this country are divided into those of chlorides, constituting 92 per cent of all reserves, and sulphates. The manufactured potassium fertilizers are, in turn, divided into chloride (potassium chloride, mixed salts) and sulphate (potassium sulphate, sulphate of potash-magnesia, potash-magnesia concentrate) ones.

The basic mineral used in the production of chloride fertilizers is sylvinite, which is a mixture (agglomerate) of sylvite (KCl) and halite (NaCl), containing 12-15% K_2O. Sulphate fertilizers are produced from the minerals of kainitic, langbeinitic, and mixed langbeinitic-kainitic ores,

as well as from alunites. The chemical composition of some potassic minerals is as follows: carnallite, $KCl \cdot MgCl \cdot 6H_2O$; kainite, $KCl \cdot MgSO_4 \cdot 3H_2O$; schoenite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$; langbeinite, $K_2SO_4 \cdot 2MgSO_4$; polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot CaSO_4 \cdot 2H_2O$; alunite, $(K, Na)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$; and nepheline concentrate, $(K, Na)_2O \cdot Al_2O_3 \cdot 2SiO_2$. Complete processing of the latter yields alumina, cement, soda, and potash. After magnesium is extraced from carnallitic ores, a fertilizer known as potassium chloride electrolyte comes as a by-product.

Potassium fertilizers are classified as concentrated (potassium chloride, potassium sulphate, potassium chloride electrolyte, potassium salt, sulphate of potash-magnesia, potash-magnesia concentrate) and raw (sylvinite, kainite) salts.

Potassium chloride (KCl) is the main potassium fertilizer accounting for 80 to 90 per cent of the total production of these fertilizers. It contains 53.7-60.0% K_2O and not more than one per cent of moisture. It is a crystalline friable substance of pink or white colour with a shade of grey.

Potassium chloride is produced in two processes: flotation and halurgical.

Flotation is used to produce potassium chloride from sylvinitic ores. The process resides in separation of KCl and NaCl after removal of the silt. The separation of minerals (sylvite KCl and halite NaCl) by flotation is based on their different wettability. Ground ore is agitated in water or in an aqueous solution with addition of fatty amines, then air is passed through the pulp so that it forms small bubbles. Particles of the hydrophobic mineral sylvite adhere to the air bubbles and rise to the surface of the pulp in the form of froth. The froth contains concentrated KCl which is dehydrated on a centrifuge and sent for drying.

Particles of the hydrophilic mineral halite accumulate on the bottom of the flotation cell and are discharged through an opening.

The halurgical process of potassium chloride production from sylvinitic ore is based on the different solubility of KCl and NaCl in water. The dissolution is carried out at 90-100 °C with subsequent cooling of the solution to 20-25 °C. In solutions saturated with both salts, the KCl

content becomes almost twice as high, when the temperature is raised from 20-25 to 90-100 °C, while that of NaCl decreases. When such a solution is cooled, KCl crystallizes, whereas NaCl remains in it. It is this property of salt solutions that is used in the cyclic halurgical process of potassium chloride production.

The finely crystalline potassium chloride, obtained by fine grain flotation and halurgically, tends to cake in storage, especially at particle sizes less than 0.15 mm. To avoid this inconvenience, it is granulated, or pelletized, to a granule size ranging from 1 to 3 mm. The tendency of potassium chloride to cake is also minimized by addition of amines.

Potassium sulphate (K_2SO_4) is a white fine crystalline powder containing 1.2% moisture and 46-50% K_2O (it may also be yellowish). Its tendency to cake is insignificant, and the fertilizer may be transported from the plant in bags or in bulk. It is produced by conversion of schoenite into langbeinite with addition of KCl which reacts with magnesium sulphate, yielding $MgCl_2$ and also potassium sulphate in the fertilizer.

Potassium chloride-electrolyte (KCl with impurities) is a finely crystalline powder with a yellowish tint, containing 31.6-45.5% K_2O and displaying a strong tendency to dust. It does not cake (its moisture content not exceeding 4%) and is packed into paper bags or transported in bulk.

Sulphate of potash-magnesia, or sulpomag, ($K_2SO_4 \cdot MgSO_4$) is a finely crystalline powder of greyish pink colour with a pronounced tendency to dust, or greyish pink granules of irregular shape. It contains 29% K_2O and 9% MgO and not more than 5% moisture. The fertilizer does not cake and can be transported in bulk or in paper bags. Just as potassium sulphate, it is applied to chlorine-sensitive crops.

Potash-magnesia concentrate is produced in the form of grey granules containing 1.5-7% moisture, 18.5% K_2O, and 9% MgO. It does not cake and is transported in bulk. The fertilizer is applied primarily to chlorine-sensitive crops.

Mixed 40% potassium salt (KCl + NaCl) is a grey crystalline powder including pink crystals, a mixture of potassium chloride with ground sylvinite (up to 35% NaCl). It contains not more than 2% moisture and 40% K_2O. It has a tendency

to cake and is transported in bulk. The fertilizer is most suitable for crops responsive to sodium (sugar beet, fodder and table root crops). A mixture of KCl and kainite gives a 30% potassium salt.

Natural kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$ with NaCl) has large pinkish brown crystals containing not more than 5% moisture and 10% K_2O. It does not cake and is transported in bulk.

Cement kiln dust is a by-product of the cement industry. This chlorine-free potassium fertilizer contains 10-15% K_2O, is produced in a granulated form and packed in paper bags. Potassium is present in the form of carbonates, bicarbonates, sulphates, and, to a minor extent, silicates. Cement kiln dust also contains gypsum, calcium oxide, sesquioxides, and micronutrient mixtures. It is used as basal fertilizer, particularly on acid soils occupied by chlorophobic crops.

Potash (potassium carbonate, K_2CO_3) is an alkaline potassium fertilizer good for acid soils. Calcined potash must contain 63-66.7% K_2O. It is calcined to become less hygroscopic. Potash and potassium bicarbonate ($KHCO_3$) are also found in the wood and straw ash remaining in stoves. The ash also contains small amounts of phosphates. Potassium bicarbonate contains 47% K_2O.

Sylvinite ($KCl \cdot NaCl$) is essentially ground sylvinitic ore with crystals ranging from 1 to 4 mm in size, 20 per cent of the crystals exceeding 4 mm. Its colour is pinkish brown with blue crystal inclusions. Sylvinite contains 12-15% K_2O and 75-80% NaCl. It is applied at low rates, transported in bulk, tends to cake, and is used to fertilize sodium-loving crops (sugar beet, fodder and table root crops). Because of its low potassium content, sylvinite is not recommended for long-distance haulage from the quarry.

Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$ with NaCl) is ground ore containing 12-13% K_2O, highly hygroscopic and with a strong tendency to cake; its use as a fertilizer is very limited because it does not lend itself to transportation. Carnallite is used as a raw material in magnesium extraction. Its by-product, KCl electrolyte, is a valuable fertilizer.

Since the chlorine present in potassium fertilizers produces a negative effect on some crops, one must know its content and the potassium fertilizers containing it. For

instance, the chlorine content (in kg) per kg K_2O is as follows: 4.0 to 5.2 in sylvinite, 3.0 to 3.3 in carnallite, 1.4 to 1.9 in potassium salt, 0.9 to 1.0 in potassium chloride, and 0.02 to 0.1 in potassium sulphate and potash-magnesia fertilizers.

7.3 Interaction of Potassium Fertilizers with the Soil

Potassium fertilizers are readily soluble in water. However, when they are incorporated into the soil, the potassium ion immediately interacts with the colloidal particles in it, undergoing physicochemical (exchange) and non-exchangeable adsorption. It has been established that non-exchangeable adsorption (fixation) of potassium in the soil is virtually over within 24 hours after application of potassium fertilizers, hence, it is almost independent of the time between their incorporation and seeding (planting) of crops.

The exchange adsorption of potassium ions in the soil accounts for a major portion (at least one quarter) of the total exchange capacity. The reaction of physicochemical (exchange) adsorption of K^+ in the soil is reversible:

$$\begin{matrix} \text{Soil} \begin{matrix} H \\ H \\ Ca \\ Mg \\ Al \\ Mg \\ H \\ Ca \\ H \\ H \end{matrix} \end{matrix} + 9KCl \rightleftharpoons \begin{matrix} \text{Soil} \begin{matrix} K \\ H \\ KK \\ Mg \\ KKK \\ KK \\ H \\ Ca \\ H \\ K \end{matrix} \end{matrix} + 2HCl + CaCl_2 + MgCl_2 + AlCl_3$$

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl$$

As can be seen from the above reaction, the soil is acidified not only by H but also Al ions appearing in it.

As potassium cations are being exchangeably adsorbed in the soil, they displace an equivalent number of other cations (hydrogen, aluminium, calcium, magnesium, manganese, etc.) from the layer of compensating ions in the

absorbing complex of the soil, which affects the reaction of the soil solution and, consequently, the plant growth conditions. By their nature, all potassium fertilizers are physiologically acidic: plants take up the potassium cation from their aqueous solutions at a much faster rate, as compared to the accompanying Cl^- or SO_4^{2-} anion. During the interaction with the absorbing complex of the soil, the acidifying effect of potassium fertilizers on the soil solution is also manifest, especially in acid (unlimed) soils. As a result of the exchange reactions in the soil solution, either hydrochloric or sulphuric acid is formed, depending on the type of the potassium fertilizers used (chloride or sulphate). Besides, the soil solution is additionally acidified by the hydrochloric acid forming in the hydrolysis of aluminium chloride. Therefore, on acid soddy podsolic soils, potassium fertilizers are not as effective. However, the acidifying effect of potassium fertilizers on the soil solution is much less pronounced than that of ammonium nitrate and ammonia fertilizers. The results of 28 years of application of various forms of potassium fertilizers to soddy podsolic heavy loam (Central Experimental Station of the USSR Research Institute of Fertilizers and Agronomical Soil Sciences) have not revealed any difference in acidity of the soil solution in comparison with the control tests (without fertilizing).

On light soils, the acidifying effect of potassium fertilizers is more pronounced.

Non-exchangeable adsorption (fixation) of the fertilizer potassium in various soils may constitute a high percentage of the applied amount (up to 80%). For example, according to Pchelkin, fixation of the fertilizer potassium in soils varied from 14 to 82 per cent, depending on their mineralogical composition and fertilizer rate. In an experiment with ^{40}K, 63 and 70 per cent of the fertilizer potassium remained unused by plants in soddy podsolic sandy loam and heavy loam, respectively, by the end of the vegetation period, only one sixth to one eight of that amount being represented by the mobile form. Fixed potassium cations are less readily available to plants and, in some cases, fixation adversely affects their nutrition. Non-exchangeable adsorption of potassium is typical of clayey minerals of the montmorillonite and hydromica groups, having a three-layered expand-

ing lattice. The non-exchangeable adsorption capacity is particularly pronounced in vermiculite. Minerals of the kaolinite group with their two-layered lattice usually are not capable of fixation. Therefore, the amount of potassium fixation by soils is strongly dependent on their mineralogical composition: the higher the content of montmorillonites and hydromicas in a soil, the greater the degree of potassium fixation in it. Light soils (sand and sandy loam) usually fix less potassium than moderately and especially heavily loamy soils. The fixation mechanism can be explained in the following manner: cations penetrate the interstack spaces when the dimensions of the latter are maximum (in the expanded state) and occupy the hexagonal voids in the network of oxygens of the tetrahedral layers, attracting both negatively charged oxygen layers with the result that the cations find themselves in a closed space. This is how cations having a radius of 0.130 to 0.165 nm (NH_4^+, Rb^+, Cs^+) are adsorbed. Potassium is one of such cations (with a radius of 0.133 nm). Desiccation of the soil, especially when it alternates with moistening (which often happens in the field), may intensify the potassium fixation process considerably, although it takes place in moistened soil as well. Therefore, potassium fertilizers must be incorporated deep into the arable layer and not into the surface layer which is often parched.

When coarse-grained crystalline or granulated potassium fertilizers are applied, the non-exchangeable adsorption of potassium in the soil decreases (by about 20-30%) because of the smaller area of their contact with the soil, as opposed to fine-grained ones. As was shown in the experiments conducted at the USSR Research Institute of Fertilizers and Agronomical Soil Science, the form of potassium fertilizers produced almost no effect on the amount of fixation of their potassium by the soil. As more potassium fertilizers are applied, the absolute quantity of potassium fixed by the soil increases, while the relative one, expressed as percentage of the applied amount, decreases. As has already been mentioned, some soils exhibit a greater capacity to fix potassium. For example, according to Pchelkin, slightly leached chernozem (Sumy experimental station) fixed 144 mg K_2O per 100 g of soil after application of 30 t K_2O per

hectare. Hence, a hectare of such soils can non-exchangeably adsorb up to 4320 kg K_2O. For soils to become saturated with potassium to such an extent will take centuries if it is borne in mind that only 50 per cent of the fertilizer potassium are utilized by plants. There is evidence to the effect that the rate of fertilizer potassium fixation by the soil decreases with pH and increases when the soil is limed.

In this case, if the degree of potassium saturation of the soil as a result of liming does not go beyond 80 per cent, then the mobility of potassium increases due to liming, and if $V\%$ exceeds 80 per cent, the mobility decreases.

On soils richer in humus, the liberation of fixed potassium is hindered because of formation of a thicker film of the humic substance on the surface of colloids, which does not allow potassium to be displaced from the crystal lattice of minerals.

When potassium fertilizers are applied systematically over a long period of time and the potassium balance is positive (i.e. when the amount of the potassium applied with fertilizers by far exceeds that removed by crops), the content of mobile forms of potassium and its non-exchangeable (acid-soluble) forms goes up. Here, the exchangeable potassium increases in quantity to a greater extent than the water-soluble one. As far as its transition to a non-exchangeable state is concerned, there are many factors involved, and its degree may be quite impressive.

The interaction between different potassium compounds in the soil may be expressed as follows:
crystal lattice potassium $\rightleftarrows$ non-exchangeable potassium $\rightleftarrows$ $\rightleftarrows$ exchangeable potassium $\rightleftarrows$ soil solution potassium.

In the final analysis, plants may take up all forms of soil-derived potassium but in different amounts, 101 years of experimentation on a loamy soil (England) have shown that crops removed, when harvested, three to four times more potassium as compared to its content in exchangeable form. These and many other findings corroborate the possibility of uptake of non-exchangeably adsorbed potassium by plants. According to some investigators, the intensity of cropping influences the amount of potassium fixation by the soil.

The pattern of interaction between fertilizers and the

absorbing complex of the soil is indicative of negligible migration of potassium across the soil, with the exception of sandy and sandy loam soils. As a rule, on soils of moderately heavy and heavy texture, the fertilizer potassium is not leached below the 0-40-60 cm layer, that is, it virtually remains in the root zone and, being exchangeably adsorbed in the soil, is available to plants. As suggested by the results of lysimeter experiments, the annual rate of K_2O leaching from the loamy soils of the Non-Black Earth zone ranges from 0.4 to 7 kg/ha, the rate of leaching from sandy loam being 12 kg/ha. More sizable potassium losses (up to 40 kg/ha per annum) have been observed on red soils. Because of the minimal potassium migration, potassium fertilizers should not be incorporated into the uppermost soil layer in view of the fact that roots penetrate deeper in search for moisture. Furthermore, the upper layer prone to desiccaton will fix potassium to a greater degree. The presowing application of potassium fertilizers to all tenacious soils should be performed during ploughing in autumn, and only in the case of light (sandy and sandy loam) soils with sufficient and excess moisture potassium can be applied in spring. Due to shallow placement, potassium fertilizers used for dressing are often less effective than those applied at once before sowing at full rate.

7.4 Application of Potassium Fertilizers to Farm Crops

Potassium fertilizers are selected according to soil texture, mobile potassium content in the soil, moisture content, crops, their desired yields and also quality. They are particularly effective on sandy soils, soddy podsolic sandy loam, peat-body and flood plain, yellow and red soils. Potassium fertilizers are highly effective when applied in high-rainfall regions to soddy podsolic loam, grey forest soils, podsolized and leached chernozems—if these soils have a medium or low mobile potassium content. The role of potassium also increases on the old-arable irrigated sierozems of Central Asia with intensive cultivation of cotton. The effectiveness of potassium fertilizers is low

or even nil in most cases involving typical, ordinary and southern chernozems, takyr-like and grey-brown soils, and sierozems. Potassium fertilizers are not applied to alkaline soils because they increase soil alkalinity and may lower crop yields.

A summary of the results of 689 field experiments conducted in 1965-1975 on soddy podsolic soils in the Byelorussian SSR has shown that the yields of grain crops increased to 60-70 kg of grain per mg K_2O in 100 g of soil up to a 14-20 mg content of mobile potassium in 100 g of soil. With K_2O contents exceeding 20 mg per 100 g of soil, the yields of cereals increased but insignificantly (on loamy soils) or even sharply decreased (on light soils). According to Kulakovskaya, the exchangeable potassium content ranging from 18-20 mg per 100 g of soil in light soddy podsolic soils to 23-25 mg per 100 g in loamy soils may be considered optimal to guarantee desired cereal yields with a high grain quality.

Potassium fertilizers are most effective when used in an optimal ratio to nitrogen and phosphorus fertilizers. They can be used without the other two only on reclaimed peat bogs and peat-boddy soils adequately supplied with other nutrients.

As has already been mentioned, it is most advisable to apply potassium fertilizers to tenacious soils at full rate (except for a small amount to be drilled under some crops) during ploughing in autumn, without dressing. When chlorine-containing potassium fertilizers are applied in autumn, chlorine is leached out by autumn and spring rains from the root zone of the soil without harming chlorophobic crops. If potassium fertilizers cannot be applied in autumn, they should be placed during reploughing in spring, although in that case chlorine-containing fertilizers may produce a negative effect on crops sensitive to chlorine. Potassium fertilizers should be applied in spring only to sandy and sandy loam as well as peat-boggy and flood plain soils. In the case of light soils, especially under irrigation, it is advisable to use them partially for dressing (row crops).

The crops with highest potassium requirements include sunflower, tobacco, vegetables, sugar beet, fodder root

crops, potato, fruit and ensilage crops. It is these crops that should be treated with potassium in the first place. However, tobacco, grape, fruit and citrus crops, some vegetables (especially those grown in greenhouses), buckwheat, potato, flax, medicinal herbs, and essential-oil crops must be treated with chlorine-free potassium fertilizers, otherwise their quality may suffer seriously (tobacco leaves become less combustible, flax fibres become of poorer quality, and potato tubers become less starchy). If applied in autumn, the harmful effect of chlorine in potassium fertilizers is eliminated for most crops.

Grain cereals, sugar beet, fodder root crops, table beet, and most fodder crops display almost no adverse response to chlorine-containing potassium fertilizers and have even higher yields than in the case of chlorine-free fertilizers.

Of primary importance for sugar beet and fodder root crops are potassium fertilizers containing sodium, that is, in this case, even raw salts or their mixtures with KCl can be used with success.

As regards chlorine-sensitive crops, one must select those potassium fertilizers that have as low a chlorine content as possible, if chlorine-free fertilizers are not available. For example, potatoes should best be treated with potassium sulphate, sulphate of potash-magnesia (schoenite), or potash-magnesia concentrate, rather than potassium chloride. Potassium salt and even kainite should not be used to treat potatoes because of their high chlorine content*.

Limed (calcareous) soils, especially those occupied by flax and potatoes, require higher rates of potassium fertilizers because of the antagonism between the potassium and calcium ions taken up by the plants.

The factor of fertilizer-potassium utilization by plants varies widely (from 12 to 50%) depending on the crop, soil, and climatic conditions. Usually, the uptake of fertilizer-potassium during the first year is around 40 per cent. A higher potassium utilization factor is typical of row crops requiring more of this nutrient.

* The results of experiments with potatoes in different regions indicate that application of chlorine-containing potassium fertilizers reduces the yield of starch by 7 to 15 per cent, as compared to chlorine-free forms.

The best ways to enhance the effectiveness of potassium fertilizers are as follows: optimal distribution of their reserves among the different native zones of the country, predominant application of these fertilizers to crops characterized by intensive potassium uptake, combining potassium fertilizers with nitrogen and phosphorus ones and, if necessary, with liming, and rational use of potassium fertilizer forms.

Analysis of the experimental data provided by the Geographical Network has made it possible to define, from soil and climatic conditions, regions most suitable for potassium fertilizers in terms of their effectiveness.

Years of experimentation at Soviet experimental stations suggest that application of a centner of K_2O in fertilizers increases the yield of grain by 2 to 3 centners, potatoes by 20 to 33 centners, sugar beet by 35 to 40 centners, seed cotton by 1 to 2 centners, flax fibre by 1 to 1.5 centners, hay of cultivated grasses by 20 to 33 centners, and hay of meadow grasses by 8 to 18 centners per hectare.

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